RESEARCH HIGHLIGHTS

2002 - 06

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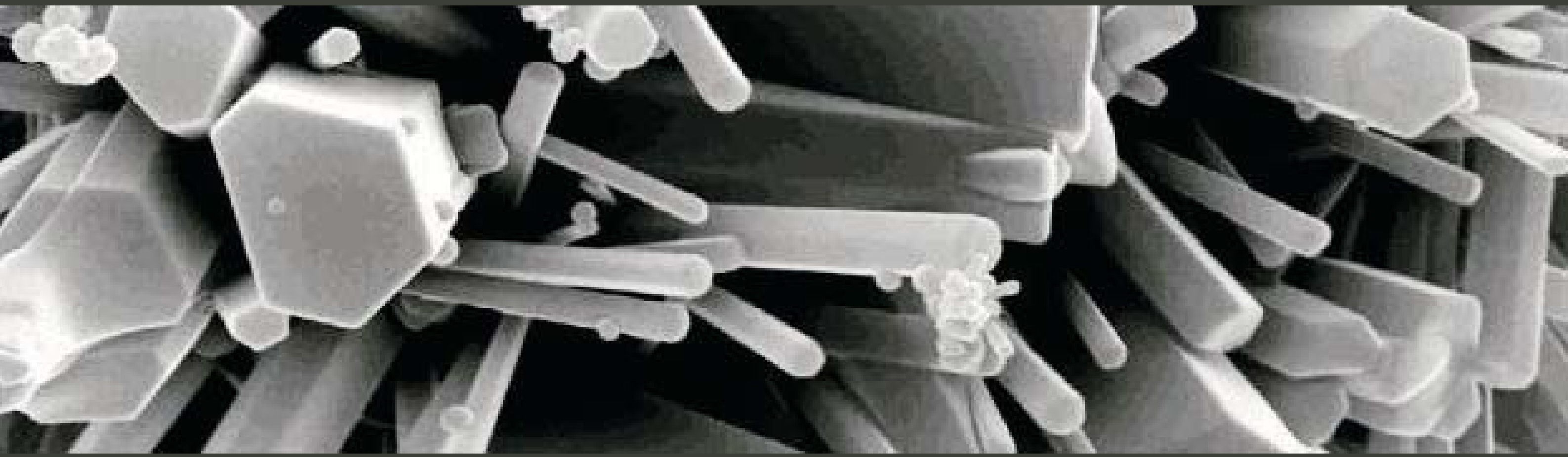
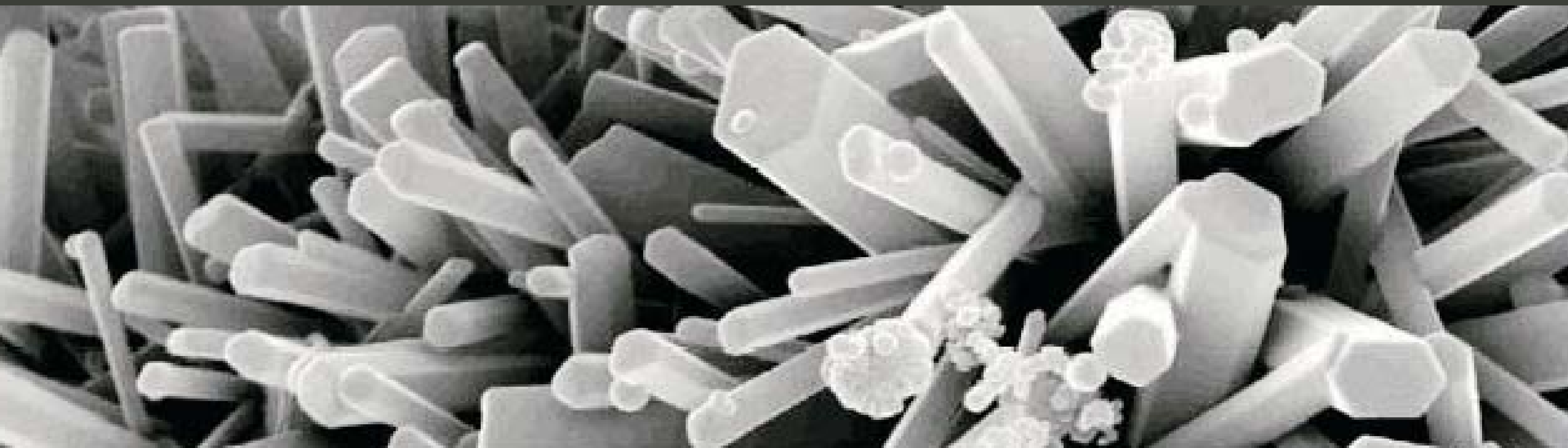
Contents





A Word from the Directors

Five years have passed since the associate laboratory CICECO was created in March 2002 at the University of Aveiro, Portugal, with the mission of developing the scientific and technological knowledge necessary for the innovative production and transformation of ceramics and composite materials. CICECO is now a mature institute, with European status. These research highlights present some of the excellent work our researchers have been performing since 2002. As Directors, we are proud and honored to have had the privilege of helping make CICECO what it is today.

CICECO is the largest Portuguese institute in the field of materials science and engineering, comprising (Dec. 2006) 53 academic staff, 20 full-time researchers, 46 post-doctoral associates, 68 PhD students, and ca. 60 other students. Our main areas of expertise are: advanced micro and nano-structured materials for communications technologies; advanced materials for industrial applications; chemistry and technology of polymeric and lignocellulosic materials and biomaterials.

CICECO is also one of the most productive research institutes in the country in all scientific areas: an average publication of 4.5-5 SCI papers per year per academic staff or full-time researcher; over 1400 SCI papers (many in top journals); 27 patents published; and 71 Ph.D. theses completed in the last 5 years (2002-06). In 2006 we published 382 SCI papers, ca. 5% of all Portuguese papers (7686) quoted on the Web of Science. 10 CICECO researchers (ca. 10% of the national total) were awarded the ‘Prize for Scientific Excellence’ by the Portuguese Science Foundation.

CICECO is a truly international research centre. For example, 45% of our full-time researchers and 65% of post-docs are not Portuguese nationals. We are part of the main stream materials research in Europe. We are actively involved in the Network of Excellence ‘Functionalised Advanced materials and Engineering of Hybrids and Ceramics’, FAME, and in the INTERREG IIIB ‘Materials Network for the Atlantic Area’, or in Integrated Projects such as ‘Innovation and Sustainable Development in the Fibre Based Packaging Value Chain’. We are running the two Erasmus Mundus M.Sc. courses, the ‘Joint European Masters Programme in Materials Science’ with the universities of Aalborg and Hamburg, and a FAME programme. We hosted one of the first and very few Portuguese Marie Curie Training sites, ‘Advanced Ceramic Materials: Synthesis & Structure’.

CICECO is also commited to knowledge transfer to industry, through our Centre for Materials Design and Technology. Together with the Food Chemistry Group of the Organic Chemistry, Natural and Agrofood Products Research Unit of the Chemistry Department of the University of Aveiro, the spin-off company FoodMetric was started. Several prizes in national entrepreneurial contests were awarded to FoodMetric: first prize at ‘Concurso Nacional de Empreendedores’ and ‘2º Concurso de Criação de Empresas de Base Tecnológica de Mira’, and second prize at ‘Concurso Bioempreendedor’. FoodMetric has already obtained financial support from NEOTEC (AdI) and venture capital investors. As another example, in 2006 we started a consortium with some 6 companies, IDPoR, ‘Research and Development Platform on Polymers from Renewable Sources’. Two other similar technology platforms on ceramics and energy are being created.

CICECO is probably the best equipped institute in the country to perform research in materials science. In particular, we are the focal point of the Portuguese Electron Microscopy Network and also house the top solid-state nuclear magnetic resonance facilities. Very soon, we will also be one of the best equipped national centres for X-ray diffraction.

Aveiro, 12th July, 2007.

João Rocha

Joaquim Vieira

João Rocha

Director
CICECO
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Joaquim Vieira

Vice-Director
CICECO
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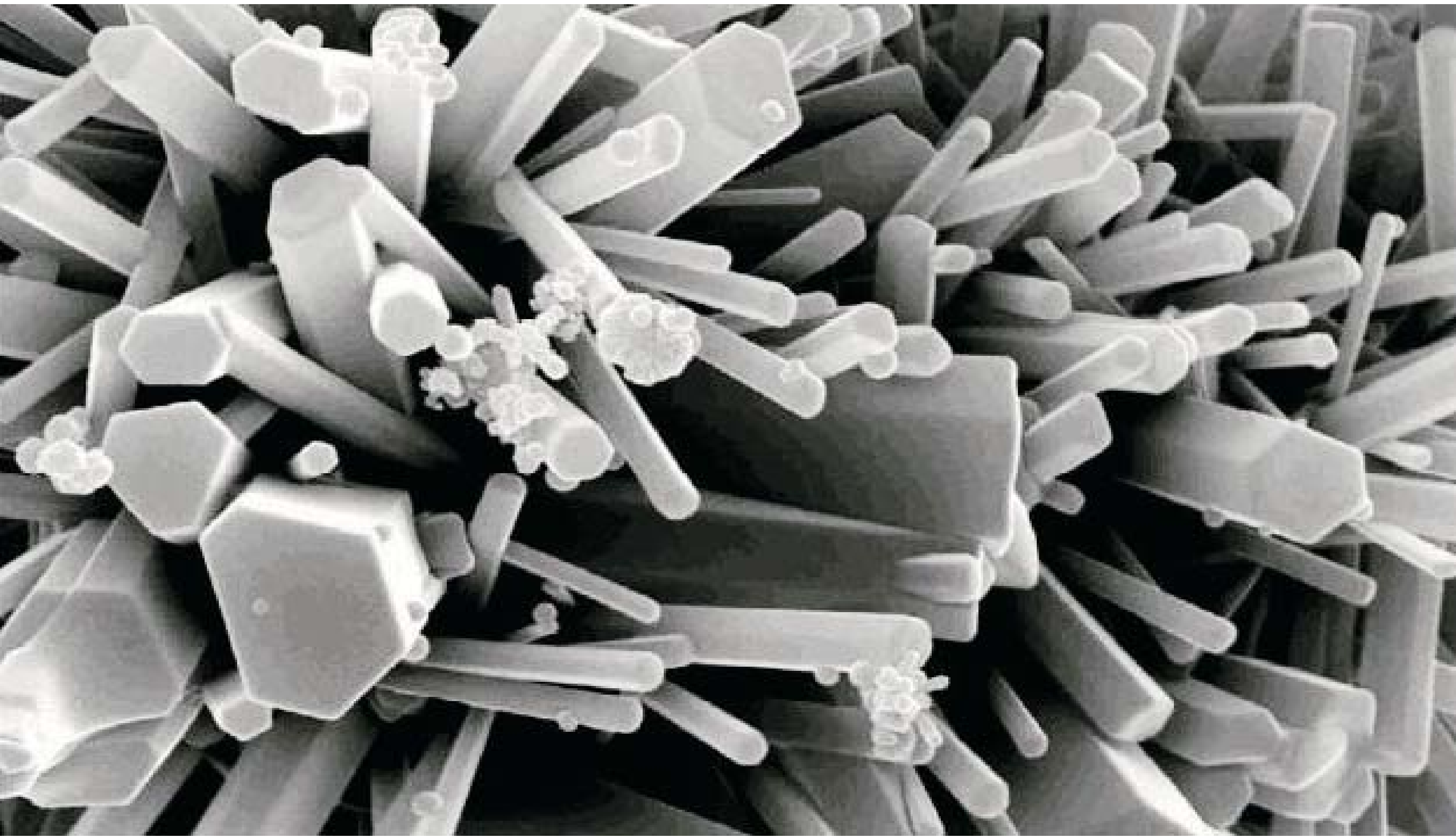

Phase Separation and Hyperfine Studies on Colossal Magnetoresistive Oxides

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The interaction between the electronic spin, charge, orbital and the lattice degrees of freedom in manganites leads to conspicuous phenomena such as colossal magnetoresistance and electric/magnetic phase separation. In the framework of a general study of manganites, we have performed particular studies dealing with a microscopic probing of phase separation, its relevance to magnetocaloric properties and the theoretical interpretation in terms of non-homogeneity statistics. Using the perturbed angular correlation (PAC) technique, a percolative transition on ferromagnetic insulator manganites from uncorrelated to correlated polaron clusters was for the first time observed. The phase separation of charge-ordered/ferromagnetic clusters in manganites was shown to allow a tailoring of the magnetocaloric effect as the entropy associated with this transformation is considerable and depends on the magnetic history of the sample. The description of the inhomogeneities and complexity in manganites was possible using the generalized Tsallis thermodynamics, which considers the non-extensivity of statistical properties in systems with long-range interactions and fractality, as in phase-separated manganites.

In this highlight a stronger emphasis is given to the hyperfine studies, using radioactive ions, implanted at ISOLDE-CERN, where the Aveiro team leads an international project (IS390-11 partners) in close collaboration with Instituto Tecnológico Nuclear and the University of Porto to perform local studies on relevant structural problems of Colossal Magnetoresistive Oxides (manganites) by doping these with suitable radioactive isotopes for Perturbed Angular Correlations and Emission Channeling. The hyperfine PAC technique allows a local probing of the samples, using the coupling of the quadruoplar and/or the magnetic moment of the implanted probe to the electric field gradients and hyperfine magnetic field on insulator and conducting samples. This provides information on the coupling between the local structure and chemical doping (by oxygen and metal vacancies), magnetic and electric properties.

The system LaMnO$_{3+\delta}$ presents a wide range of oxidative nonstoichiometry ($0<\delta<0.2$) and associated complex structural/magnetic phase diagram. A systematic ^{111m}Cd PAC study in this series was completed. A remarkable behaviour was found on the ferromagnetic insulator LaMnO$_{3.12}$ sample (Tc=145K) that presents a orthorhombic (O) to rhombohedral (R) reversible phase transition extending from 200 to 300K (x-ray diffraction). An extensive nanoscopic analysis showed the undeniable separation of two distinct local environments, consistent with a phase coexistence scenario and allowed us to study the detailed structure, stability, and evolution of the Jahn-Teller (JT)-polaron clusters in manganites. We showed (Fig. 1) that over all temperature range (10 to 800K) two main local environments (u: *undistorted*, d: *distorted*) coexist, i.e. different fractions of probes (f_u, f_d) interacting with each electric field gradient (EFG) distribution.

Above room temperature an almost axially symmetric local environment EFG$_u$ predominates while at low temperatures mainly a weaker highly asymmetric EFG$_d$ exists. The persistence, up to very high temperatures, of the d phase, is compatible with the scenario f random distributed nanoscopic regions of a highly distorted lattice (EFG$_d$) embedded in a more symmetric matrix (EFG$_u$). The EFG asymmetry of the *d* phase is the same as found in the Jahn-Teller distorted pure LaMnO$_3$ compound. The smooth temperature dependence of the fractionssuggests

Vitor Amaral was born in 1962, obtained his PhD in Condensed Matter Physics at the University of Porto in 1993 and is Professor Associado com Agregação (2005) at the Physics Department of the University of Aveiro. His main research interests are magnetism and superconductivity, particularly complex oxides and nanoparticles. He is author or co-author of more than a hundred SCI publications. He is presently Vice-President of the Portuguese Physical Society.

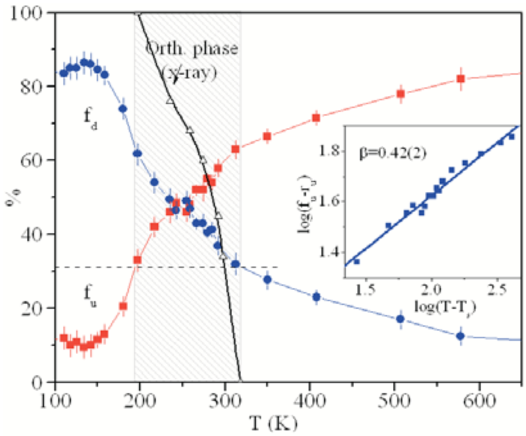

Figure 1. Fraction of probes interacting with the different EFG. The orthorhombic phase fraction obtained using x-ray diffraction technique is also shown. The dashed lines assign the percolation threshold. Inset: fu-fraction dependence on temperature.

the presence of a percolation continuous phase transition between the *u* and *d* local environment (T=Ts~Tc) with percolation thresholds ~30% assigned by macroscopic (x-ray) coexistence. The dynamics of the local deformations (Jahn-Teller polarons) was also studied through the attenuation of the spectra. This is a thermal activated process of small polarons with activation energy E_a=0.31 e V, similar to the polaron binding energy reported in the literature.

The residence time values (τ_r~0.5 μs at 270K) correspond to an ultra–slow polaron dynamics, compatible with the insulator behaviour of this sample.

The analysis of the data requires the study the localization of implanted ions. This is usually done in single crystals and epitaxial thin films using the emission channelling (EC) technique (electrons emitted by implanted probe are collected by a 2D detector). The intensity change with crystallographic directions is compared with simulated spectra for several positions of the emitting probes. Our EC results, combined with the values of the hyperfine fields, point to the position of Cd ions at La sites. Fig. 2 shows one characteristic result of EC spectra.

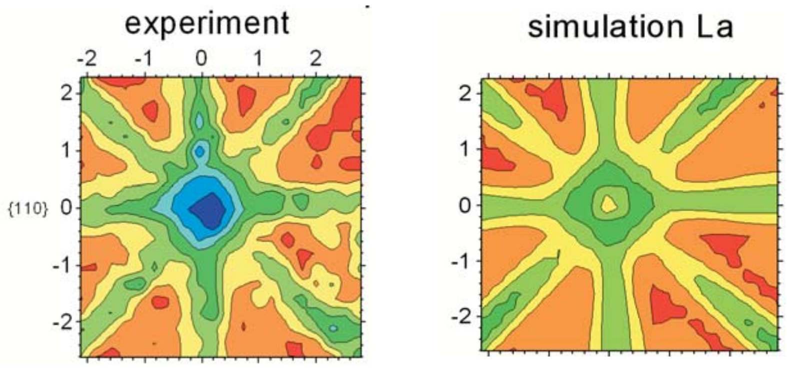

Figure 2. Experimental and simulated EC spectra for one of the observation directions (100) obtained from an epitaxially grown La-Ca-MnO_3 film. Lateral scales are angular deviations.

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Cyclodextrin Compounds: From Basic Research to Functional Materials

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Research on cyclodextrin (CD) inclusion has experienced an almost linear growth in the last 30 years. Most publications are devoted to CD encapsulation of organic compounds for applications in medicine, pharmacy or food industry. Presently, the spotlight is on the inclusion of organometallic or coordination compounds in CDs, a largely unexplored area with potential of applications, particularly, in oncology, diagnostic tests, catalysis, and non-linear optics. Our contribution to this field involves setting a comprehensive description of the structural aspects of the CD host interaction with the metal guest in solid compounds, using the plethora of techniques. This information has allowed the progress in the rational design of compounds with specific applications in catalysis and luminescence.

Cyclopentadienyl metal carbonyl complexes CpM(CO)$_n$R (M = Mo, n = 3, X = Cl, CH_2CONH_2; and M = Fe, n = 2, X=Cl) were included in native and permethylated beta-cyclodextrins (beta-CD and TRIMEB) and the resultant inclusion compounds were characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), $^{13}C\{^1H\}$ CP/MAS NMR spectroscopy and vibrational spectroscopy (FTIR/Raman). XRD was of particular use in the identification of the formation of true inclusion compounds (ICs). In most of the obtained materials, the presence of broad reflections with relatively low intensity did not allow structural refinement, so identification relied on the empirical evidence that the XRD patterns of the materials should be clearly distinct from those obtained by the superimposition of the diffractograms of each individual component. Compound TRIMEB•[CpMo(CO)$_3$Cl], interestingly, exhibited a better defined diffractogram, allowing us to perform *ab initio* optimisations of the structure in order to obtain a model of inclusion.[1] The guest CpMo(CO)$_3$Cl and TRIMEB were defined using coordinates from the corresponding crystal structures found in the literature, and treated as rigid bodies for structural modelling using global optimisation (Monte Carlo approach) with the FOX program package. The model in Fig. 1 unequivocally confirms inclusion, yet one should note that, since the molecules were treated as rigid bodies, some groups of atoms are unrealistically close, in particular the methyl groups of TRIMEB.

Compounds beta-CD-CpMo(CO)$_3$CH$_2$CONH$_2$ and TRIMEB-CpMo(CO)$_3$CH$_2$CONH$_2$ were explored as pre-catalysts for the epoxidation of cyclooctene using with tert-buthylhydroperoxide as the oxidant, and their performances were compared to that of the non-included complex CpMo(CO)$_3$CH$_2$CONH$_2$. Results varied according with the nature of the hosts,[2] showing that CDs and the solvents (if any) influence the kind of systems in which the pre-catalyst will be used. This way, the beta-CD compound has potential to be used in heterogeneous solid–liquid systems, while the TRIMEB compound is more suited to homogeneous or liquid–liquid biphasic systems.

We also investigated the potential of CDs as second sphere ligands for the fine-tuning of the luminescence properties of europium luminescent diketonates,[3] in particular Eu(NTA)$_3$•2H$_2$O with NTA = naphthoyltrifluoroacetone. Our first studies using the host beta-CD revealed that encapsulation induced emission from the singlet excited state of the ligands, with the corresponding inefficiency of the ligand-to-metal energy transfer step. This was associated with steric effects, arising from the restricted space available for the guest NTA groups in the beta-CD cavity. In fact,

Susana Santos Braga received her degree in Pharmaceutical Sciences from University of Porto in 1998 and completed her Ph.D. on the chemistry of cyclodextrin inclusion compounds at the University of Aveiro in 2003 under the supervision of Prof. J. J. C. Teixeira Dias. She carried post-doctoral work with Prof. I. S. Gonçalves at the University of Aveiro and enrolled as full-time researcher at CICECO in December 2005. She is the author of 20 papers.

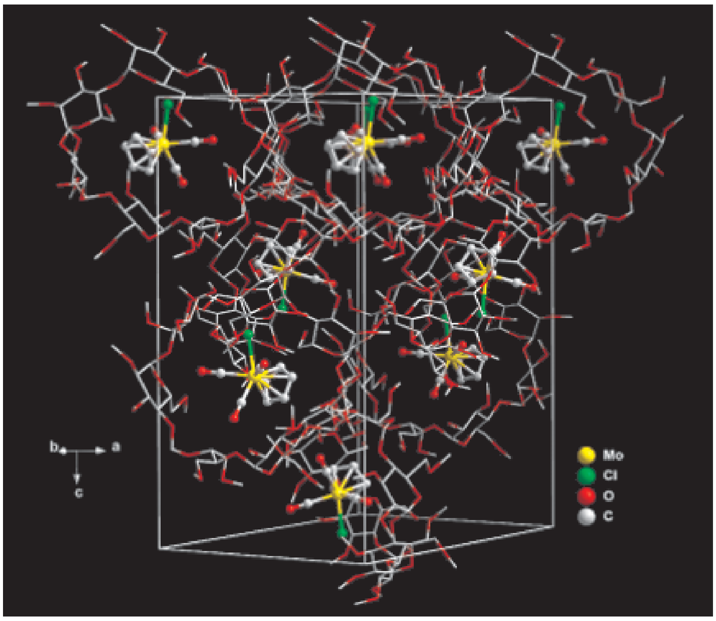

Figure 1. Unit cell contents, viewed in perspective towards the (1 7 0) plane, of the structural model obtained for TRIMEB·$[CpMo(CO)_3Cl]$. The TRIMEB and $[CpMo(CO)_3Cl]$ residues represented with the straw and ball-and-stick models, respectively.

the encapsulation of $Eu(NTA)_3 \bullet 2H_2O$ in gamma-CD, which has a cavity diameter of 7.9 Å compared with 6.2 Å for beta-CD, was shown to induce a more efficient ligand-to-metal ion energy transfer pathway.

The rational design of inclusion compounds led us to further explore the influence of host geometry by using a chemically modified gamma-CD in which the hydroxyl groups were replaced with methoxyl residues (TRIMEG). The overall shape of TRIMEG, with increased cavity opening and depth, proved to be advantageous for encapsulation of $Eu(NTA)_3 \cdot 2H_2O$ as there was a significant enhance in efficiency of the ligand-to-metal ion energy transfer observed for the TRIMEG·$Eu(NTA)_3$ compound.[4]

In conclusion, the in-depth understanding of the geometry of cyclodextrin inclusion compounds allowed us to select the most suitable CD to tailor the properties of a particular guest. Cyclodextrins have, thus, a virtually boundless potential as multi-functional hosts for tuning metal compounds into new functional materials.

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Aurivillius Perovskites: a New Approach Towards Lead-Free Piezoelectrics

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Piezoelectric ceramics have been a backbone of the multibillion transducer, sensor and actuator markets over five decades. However, the commercially available piezoelectric ceramics are all based on PZT which contains lead. As lead is going to be banned across Europe in all industrial applications in the nearest future, a great challenge exists on how to replace PZT with less toxic, more environmentally friendly materials, at the same time keeping the performance comparable with PZT.[1] Current research in this area is based on three materials classes: alkaline niobates [$(K,Na)NbO_3$)], bismuth-sodium titanates [$(Bi,Na)TiO_3$] and Aurivillius-type ferroelectrics. A breakthrough happened in 2004 when Toyota Motor Inc. announced that the textured ceramics of solid solutions based on alkaline niobates can be a replacement of PZT.[2] However, the complicated processing and texturing of these ceramics, as well as their difficult poling still pose serious problems. Our approach is to use Aurivillius perovskite ceramics [such as $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN)] where high anisotropy and poor properties can be alleviated by texturing and proper composition design.

Growth and characterization of SBT and SBN single crystals

Sufficiently big SBT and SBN crystals of high quality were needed for both texturing of bulk ceramics and fundamental property understanding in these materials with highly anisotropic structure. The growth of SBT and SBN single crystals was done by a high-temperature flux method in a specially developed home-made apparatus. The flux composition and growth conditions were modified so that big crystals (Fig. 1) of unattainable before quality were achieved.[3] Due to their layered crystal structure, the properties revealed a strong anisotropy (Fig.2) that points out to a particular crystallographic direction for maximizing the properties.[4]

Figure 1. SBT crystals grown by the modified flux method.

Textured ceramics by hot pressing

Aurivillius ceramics processed under certain conditions possess highly anisometric (plate-like) grains that can be oriented via uniaxial pressing under high temperature. The anisotropy of ferroelectric and dielectric properties studied in single crystals predicted significant improvement of the performance of textured ceramics. The study of texturing by hot forging (see Fig. 3 as an example) allowed high dielectric properties of SBN ceramics to be achieved. The dielectric permittivity parallel to grain plane was doubled as compared to random ceramics. This study paved the way for the commercialization of SBN-type ceramics as using hot forging the scaling up of the production can be easy.

Maria Elisabete J. V. Costa obtained her PhD degree from the University of Aveiro (UA) in 1997 and, since then, is an assistant professor at the Department of Ceramic and Glass Engineering of UA. Besides teaching activities and, as a member of CICECO, she is currently involved in various R&D activities. Her scientific interests are mainly focused on the study of ferroelectric materials, searching for processing/properties relationships allowing to optimize functional bulk and thin films performance. She has published around 40 technical papers in this field.

Andrei Kholkin is a principal investigator of CICECO. He co-authored ~200 papers on ferroelectric and superconducting materials. He is a coordinator of two European projects in the field of ferroelectrics and serves as an Associate Editor for Transactions on Ultrasonics, Ferroelectrics and Frequency Control of IEEE. He is a member of the Ferroelectric Committee of IEEE and was recently awarded by the Senior Member grade. He was a recipient of the 2004 “Estimulo de excellência” award of Portugal.

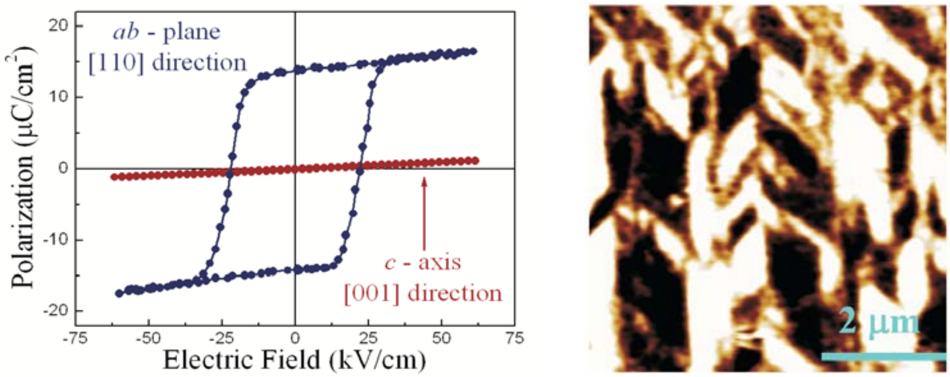

Figure 2. Record value of anisotropic polarization achieved in SBT single crystals (left) and intrinsic ferroelectric domain structure obtained for the first time in this material (right).

Textured ceramics via template grain growth

Template grain growth (TGG) is another possibility for fabricating textured ceramics: in this process a small amount of anisotropic templates (seeds) is aligned inside a matrix of relatively fine and equiaxed particles and then fired for producing a dense textured ceramics. During heating, the anisotropic template particles grow at the expense of the fine randomly oriented matrix particles increasing the volumetric fraction of highly oriented material with a specific crystallographic orientation. For facilitating the densification a liquid phase is intentionally introduced at the grain boundaries. TGG of SBT ceramics has been successfully achieved in SBT by using a small amount (5 wt%) of SBT single crystals as templates that were aligned by uniaxial pressing.[5] A microstructure with large anisometric grains was developed, followed by a significant increase in the Lotgering factor characterizing crystallographic texture (Fig. 4).

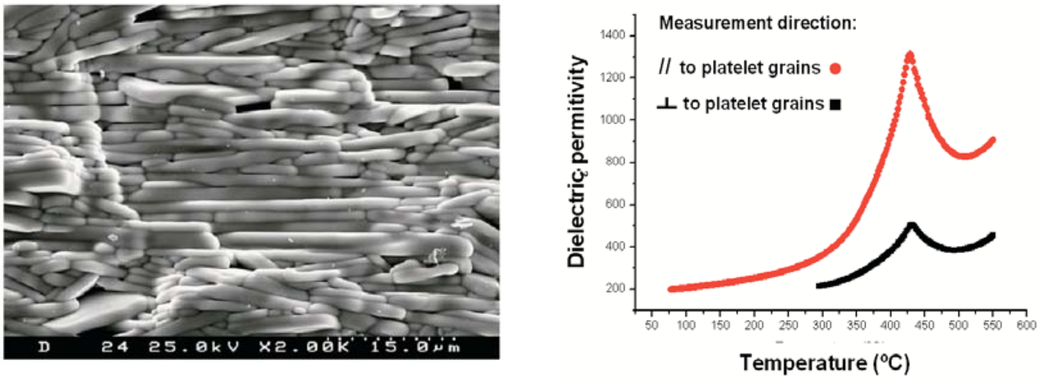

Figure 3. Grain oriented SBN ceramics (left) and improved dielectric properties along oriented grains by hot forging.

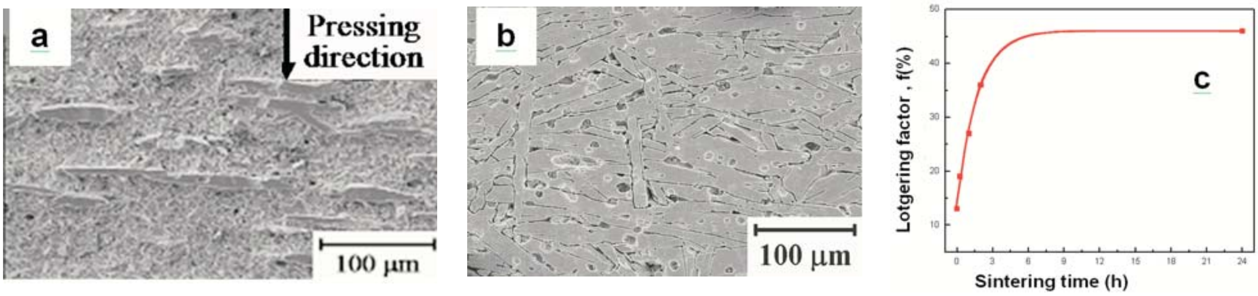

Figure 4. (a) Initial stage of TGG showing conversion of matrix to well oriented grains, (b) final state, (c) Lotgering factor as a function of sintering time.

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Magnetic Iron Oxide/Oxide-Hydroxide Nanoparticles In Organic-Inorganic Hybrid

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Recently, we have reported the synthesis of iron oxide nanoparticles (in particular ferrihydrite, maghemite and magnetite) within an organic-inorganic hybrid matrix. This matrix allows the control of the phase and of the particles size. At the same time, agglomeration is avoided since nucleation occurs at defined points and the particles are wrapped around the polymer chains. We have used these materials to investigate the origin of the magnetic anisotropy energy barrier in ferrihydrite nanoparticles and, based on a new method that compares size and energy distributions, showed the presence of uncompensated spins, randomly distributed in volume.

The interest in magnetic nanoparticles has experienced a dramatic growth in the last decade and the research comprises issues from basic research to applications, extending to biology, medicine and many other areas. In the context of biomedical applications, the iron oxides magnetite and maghemite are particularly interesting, since they are less harmful to the body than metallic nanoparticles. Relevant structural properties of nanoparticles, such as size, size dispersion, shape, organization, and interface, are better controlled when they are grown in a matrix, forming a nanocomposite. The synergy between nanoparticles and matrix leads to properties different from those of both components. In hybrid matrices, the combination of organic and inorganic components at the nanometer scale leads to materials with properties tuned between those characteristic of organic and inorganic materials.

Ferrihydrite is a crystalline iron oxide hydroxide that typically forms after the rapid hydrolysis of iron at low pH and low temperatures. Ferrihydrite is present in cold-water springs, recent bottom sediments of some lakes and soils as Hawaii basalt crusts, Spodosols and loesses. Ferrihydrite is also part of the iron cycle in living organisms. In fact, ferritin is a protein where Fe(III) is stored as ferrihydrite. The sol-gel derived di-ureasil matrix consists of a siliceous backbone covalently grafted to poly(oxyethylene) (POE) chains of two distinct average molecular weight, M_W (approximately 40.5 and 15.5 repeat units) by urea (NHC(=O)NH) cross-links. The longer polymer chains are a suitable and flexible medium to accommodate and wrap around iron oxide particles of different sizes, preventing aggregation. The urea cross-links are suitable nucleation points, leading to heterogeneous nucleation, such that the particles size is controlled by the iron content. This is reminiscent of protein ferritin whose core is wrapped up in a protein coating (Fig. 1). When using the shorter polymer chains no ferrihydrite nanoparticles form, showing the important role of the matrix in the formation of the nanoparticles.

In the magnetic properties of nanoparticles new features emerge, due to finite size and surface effects, which can dominate their behaviour. This is particularly relevant for antiferromagnetic nanoparticles (as ferrihydrite), because the total magnetic moment results from uncompensated spins, while most core spins are antiferromagnetically compensated and lead only to a minor contribution. Further

Luís António Ferreira Martins Dias Carlos (born 1964) got his Ph.D. in physics from the University of Évora in 1995 working on photoluminescence (PL) of polymer electrolytes incorporating lanthanide (Ln) salts. In 1996 he joined the Department of Physics, University of Aveiro, as Professor Auxiliar. In 1998 he became Professor Associado and in 2004 completed “Provas de Agregação” in Physics. Currently, he is Full Professor. Scientific interests: PL of (i) sol-gel derived organic-inorganic hybrids incorporating Ln ions, (ii) Ln-based micro and mesoporous silicates, (iii) Ln coordination complexes, and small-angle X-ray scattering of organic-inorganic nanostructured multifunctional materials. Luís Carlos has published over 170 SCI papers, with more than 1000 citations, and has been a regular reviewer of leading journals in Physics, Chemistry and Materials Science. He was on the Evaluation Panel for Materials Science Projects, of the Portuguese Science Foundation. He is a member of the European and Portuguese Physical Societies, Materials Research Society and European Rare Earth and Actanide Society. In 2004 he received the Portuguese Science Foundation prize for Scientific Excellence.

Vítor Amaral was born in 1962, obtained his PhD in Condensed Matter Physics at the University of Porto in 1993 and is Professor Associado com Agregação (2005) at the Physics Department of the University of Aveiro. His main research interests are magnetism and superconductivity, particularly complex oxides and nanoparticles. He is author or co-author of more than a hundred SCI publications. He is presently Vice-President of the Portuguese Physical Society.

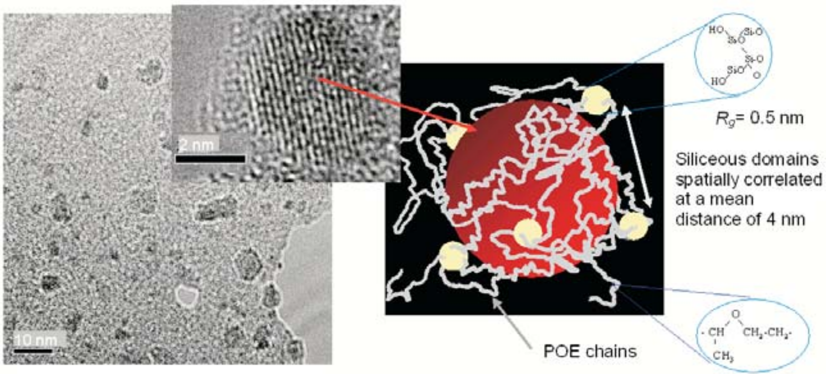

Figure 1. Electron microscopy images of the ferrihydrite nanoparticles grown inside the di-ureasil matrix and scheme of the nanoparticles wrapped around the polymer chains.

features emerge from size distribution and crystalline disorder, requiring the development of specific models. The magnetic moment dynamics (as a function of time or frequency in alternate fields) is ruled by the presence of an energy barrier due to magnetic anisotropy. This barrier determines the blocking temperature, below which the magnetic moment of each particle is 'frozen'. The analysis of the relation of particle size (r) distribution, as determined from TEM, and the anisotropy energy barrier (E) distribution, has shown that E ~$r^{3/2}$ or, as a function of volume, E ~$V^{1/2}$. This relation can be checked by the scaling of both distributions. This result contrasts with the situation in ferro or ferrimagnetic particles, where the energy barrier is proportional to the particle volume, and indicates the existence of uncompensated spins randomly distributed in volume. We have also developed a method to derive the temperature variation of the core susceptibility and of the magnetic moment based on scalin considerations. Applying this method to ferritin (which, being a protein, has a low size distribution) we showed the relevance of a magnetic moment distribution, that can be very different from size distribution in antiferromagnetic nanoparticles.

We expect that these methods may be used in other nanoparticles systems to study the way the uncompensated spins may be controlled by the modification of the oxide, the surface ligands, and growth conditions in the composite and, therefore, the magnetic properties of the composite.

This work is part of the Ph.D. thesis of Nuno João Silva and was performed in collaboration with researchers form Universidade de Trás-os-Montes e Alto Douro (Vila Real, Portugal), Instituto de Ciencia de Materiales de Aragón (Zaragoza, Spain), Institute for Rock Magnetism (Minnesota, USA), Universidad de Vigo (Vigo, Spain) and Instituto de Química/UNESP (Araraquara, Brasil).

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Photoluminescent Hierarchically-Structured Organic-Inorganic Hybrids

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In 2006, we have reported the first example of a hierarchically-structured bilayer amide cross-linked alkylene/siloxane hybrid (Fig. 1a-b) showing a thermally-actuated photoluminescence memory effect induced by the reversible order-disorder phase transition of the alkylene chains.[1] Self-assembly mechanisms are decisive for the emergence of this memory effect and the hybrid photoluminescence senses a nanoscopic scale, in contrast with the customary case for which it is determined by the dynamics of the local environment around the emitter probe.

Complex structures, such as living organisms or highly structured materials, share in common the fact that their inherent complexity may be accounted for by the tangled organization of a vast number of simple units. The complex behaviour arises not necessarily due to the atomic structure of the system, but to the orderly assembly of all, or part, of its constituents. Self-assembly of synthetic soft-matter components, such as polymers, liquid crystals, surfactants, colloids and organic/inorganic hybrids results in fascinating regular hierarchically-organized structures.

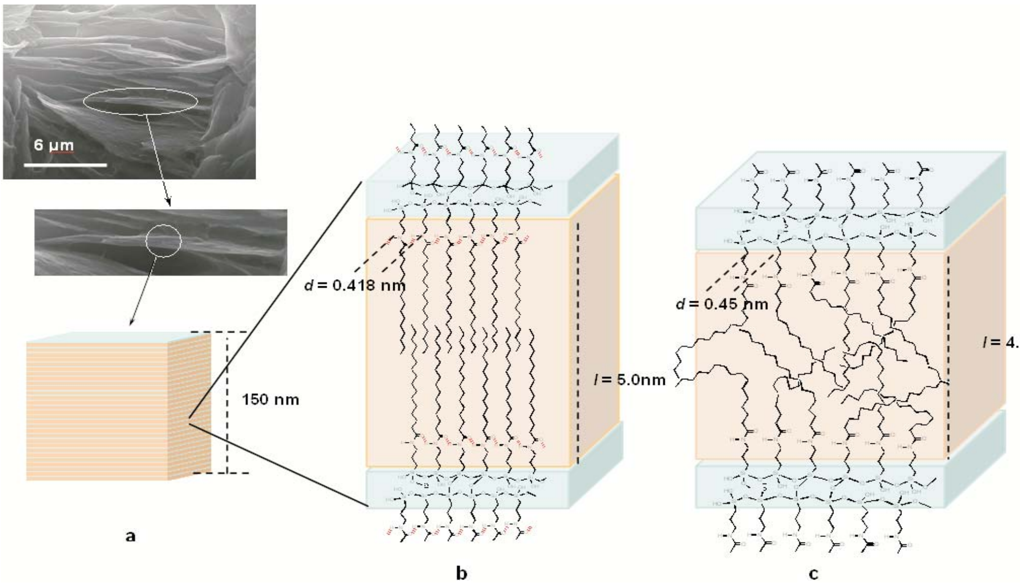

Figure 1. SEM image and schematic representations of the structure of mono-amidosil hybrid. (a) Lateral portion of a crystallite composed of a stack of bilayers. (b-c) Bilayer at room temperature and at 120 ºC, respectively.

Luís António Ferreira Martins Dias Carlos (born 1964) got his Ph.D. in physics from the University of Évora in 1995 working on photoluminescence (PL) of polymer electrolytes incorporating lanthanide (Ln) salts. In 1996 he joined the Department of Physics, University of Aveiro, as Professor Auxiliar. In 1998 he became Professor Associado and in 2004 completed "Provas de Agregação" in Physics. Currently, he is Full Professor. Scientific interests: PL of (i) sol-gel derived organic-inorganic hybrids incorporating Ln ions, (ii) Ln-based micro and mesoporous silicates, (iii) Ln coordination complexes, and small-angle X-ray scattering of organic-inorganic nanostructured multifunctional materials. Luís Carlos has published over 170 SCI papers, with more than 1000 citations, and has been a regular reviewer of leading journals in Physics, Chemistry and Materials Science. He was on the Evaluation Panel for Materials Science Projects, of the Portuguese Science Foundation. He is a member of the European and Portuguese Physical Societies, Materials Research Society and European Rare Earth and Actanide Society. In 2004 he received the Portuguese Science Foundation prize for Scientific Excellence.

Maria Rute de Amorim e Sá Ferreira André (born 1974) got her Ph.D. in physics from the University of Aveiro in 2002 working on local structure and photoluminescence features of organic-inorganic hybrids modified by lanthanide ions. From 2003 she is working at CICECO Associated Laboratory at University of Aveiro as Assistant Researcher. Her current scientific interests include local structure, photoluminescence features of sol-gel derived organic/inorganic hybrids and silicate materials incorporated lanthanide ions, lanthanide complexes and the modelling of the respective emission recombination mechanisms. Her interests are also related with wave guiding properties, photonics and integrated optics applications of organic-inorganic hybrids. She is co-author of over 70 papers.

The self-assembly of the hierarchically-structured bilayer amide cross-linked alkylene/siloxane hybrids (named mono-amidosils) is driven by i) intermolecular hydrogen bonding between amide groups; ii) van der Waals interactions between all-trans alkylene chains assuming a partially interdigitated packing mode and iii) entropic term related to the phase separation between the alkylene chains and the siloxane nanodomains.

The order-disorder phase transition involves ~30 lamellae (coherence length of ~150 nm) and its reversibility is attained through a heating/cooling cycle operating between room temperature and 120 ºC; the order-disorder phase transition temperature depends on the length of the alkylene chains. A concomitant hysteretic behaviour of the emission energy emerges from that order-disorder phase transition. However, due to the slow kinetics of the formation of the hydrogen-bonded amide-amide network on cooling, the recovery of the emission energy is achieved only after ~300 h, following a logarithmic time dependence. Thus, the mono-amidosil photoluminescence is responsive to the annihilation/formation of the hydrogen-bonded amide-amide array during the reversible order-disorder phase transition, clearly displaying a sensitivity with a nanoscopic nature, in contrast with the customary case for which photoluminescence is determined by the dynamics of the local environment around the emitter probe.

Indeed, photo-induced proton-transfer between donor-acceptor (D-A) pairs, such as NH$^+$ and N$^-$ defects, has been proposed as the mechanism responsible for the NH-related component in similar organic/inorganic hybrids.[2-4] The annihilation of the hydrogen-bonded amide-amide array delocalizes the proton, favouring the photo-induced transfer between NH-based defects. [3,4] This raises the transition probability and, hence, the emission intensity. The increase of the emission quantum yield measured after the thermal cycle, relatively to its initial value (from 7.2 to 3.0%, respectively), strongly supports this interpretation. Moreover, the delocalization of the proton also contributes to increase recombinations between distant D-A pairs (which have smaller probability) with the concomitant decrease of the emission energy. Moreover, the unusual emission energy logarithmic time dependence reflects the hierarchically constrained dynamics of the two main length-scale entities: hydrogen-bonded amide-amide arrays and hydrocarbon chains interacting through van der Waals packing; additionally supporting that the photoluminescence is not just governed by a microscopic characteristic time of independent entities, but by D-A recombinations processes occurring at larger length scales.

Main collaborators of this work: J. Rocha, V. S. Amaral, N. J. O. Silva (Aveiro) and V. de Zea Bermudez (UTAD Vila Real).

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Highly Selective Pulp Oxygen Delignification Employing Polyoxometalates

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Bleaching is a basic process in pulp and paper industry, applied to remove the residual lignin and to reach desirable brightness of cellulosic pulp. This process should be selective with respect to the lignin oxidation in order to preserve the mechanical properties of bleached pulps. Nowadays, chlorine-based bleaching chemicals possessing a negative environmental impact are progressively substituted by oxygen-based reagents (O_2, O_3, H_2O_2). Particularly, molecular oxygen is a cheap, non-toxic, renewable and widely available reagent that presents an excellent alternative to undesirable chlorine-based chemicals. However, the selectivity of lignin autoxidation in lignocellulosic materials, and particularly in unbleached pulps, by molecular oxygen is a serious scientific and technical problem.

At the Department of Chemistry of the University of Aveiro (Group of Lignocellulosic Materials belonging to CICECO) was developed a new highly selective catalytic approach for the delignification of pulps employing polyoxometalates (POMs). POMs, having an energetic barrier to lignin oxidation lower than that of dioxygen, oxidizes the lignin via electron-transfer mechanisms and then, the reduced POM is re-oxidized by O_2 (Fig. 1). The final products of the lignin oxidation and the oxygen reduction are carbon dioxide and water, respectively. The oxidation of lignin and re-oxidation of POMs occur in one stage (aerobic oxidation of lignin in the presence of POM). As bleaching liquors can be continuously re-used, POM based oxidation processes are considered as a very promising approach towards Total Effluent Free (TEF) bleaching plants.

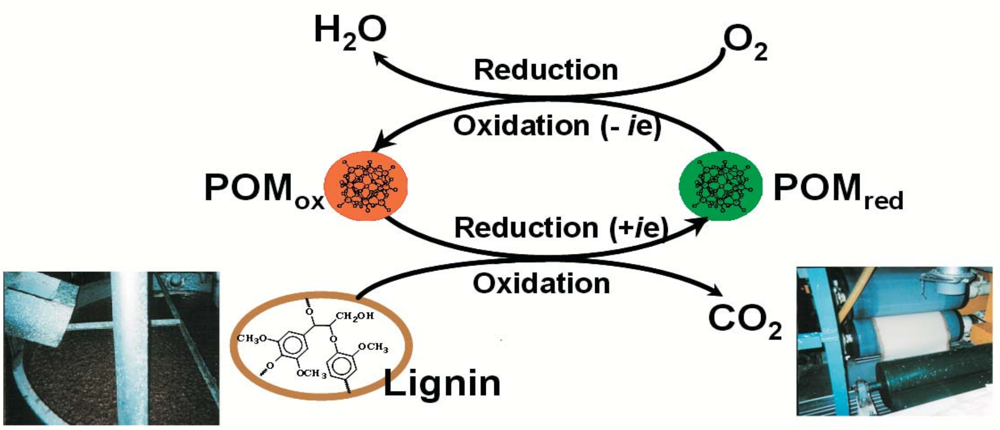

Figure1. Scheme of POM catalyzed oxygen delignification (POMs are presented as Keggin compounds in ball-and stick representation).

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Dmitry V. Evtuguin is Associate Professor at the Department of Chemistry of the University of Aveiro since 2001. Graduated in Engineering and Chemical Technology, specialty Chemical Processing of Wood, by the Leningrad Forest Technical Academy (LFTA), USSR (1985). Candidate of Chemical Science (PhD) in Chemistry (Wood Chemistry) by LFTA, USSR (1988). Author/ co-author of 95 articles and book chapters, 145 conference communications and 4 patents.

Among POM varieties, heteropolyanions of Keggin and sandwich-types have been used for delignification purposes. Particular attention has been paid to the following heteropolyanions (HPAs): $[XM_{12-n}V_2O_{40}]^{(m+n)-}$ (where X= P, Si; M= W^{VI}, Mo^{VI}; n= 1-6); $[XW_{11}M(H_2O)O_{39}]^{n-}$ (X= P, Si, B; M= M^{III}, Cu^{II}, Fe^{III}, Co^{III}, Ru^{IV}, Ni^{III}); $[(PW_9O_{34})_2Mn^{II}_{(4-n)}Mn^{III}_n(H_2O)_2]^{(10-n)-}$ (n=1,3). The technical feasibility of POM-catalysed oxygen delignification was confirmed during pilot plant experiments. Much higher selectivity and the degree of delignification were reached when compared to conventional oxygen-alkaline delignification.

A series of POMs, showing highly selective lignin oxidation, cannot be directly re-oxidised by dioxygen even at high temperatures (such as $[SiW_{11}Mn^{III}(H_2O)O_{39}]^{5-}$ and $[SiW_{11}V^{V}O_{40}]^{5-}$) thus preventing any practical application. A solution to break the thermodynamic barrier in POMs re-oxidation with oxygen was found via biocatalysis with laccase – lignolytic enzyme of oxidase family (p-diphenol:oxygen oxidoreductase, EC 1.10.3.2). In the polyoxometalate-laccase (POM/L) system, like with known organic mediators, POM oxidises the residual lignin in pulp and reduced POM is re-oxidised with laccase at the same process step (Fig. 2). Unlike organic mediators, POM is stable during the pulp treatment in the presence of laccase and can be re-used. The recent advances include the development of polyoxometalate-laccase integrated system (PLIDS) for the continuous delignification of eucalypt kraft pulp. In this case, pulp is delignified in a reactor containing POM under atmospheric pressure and the re-oxidation of withdrawn reduced POM with laccase occurs in a separate aerated bioreactor coupled with an ultrafiltration tubular ceramic membrane device allowing the separation of laccase from re-oxidized POM, which is supplied in turn continuously to the delignification reactor. Almost 70% of pulp delignification was reached in one stage with less than 15% loss of pulp intrinsic viscosity.

The interest for the mill application of new oxygen delignification system was expressed by leading industrial groups in the area, national (PORTUCEL/SOPORCEL) and European (Kvaerner Pulping AB, Sweden and Stora-Enso, Finland).

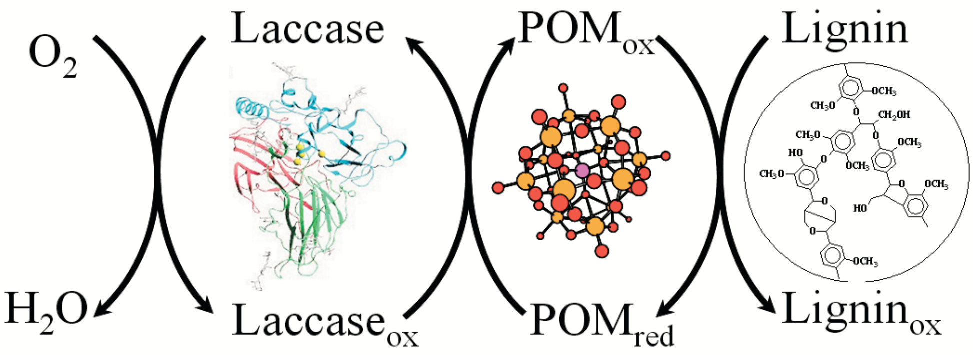

Figure 2. Scheme of the oxygen delignification catalyzed by POM and laccase.

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Contribution of Extended Defect Structures to Fast Oxygen Ion Transport

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Defects are responsible for the high oxygen ionic conductivity observed in oxides with application in high temperature electrochemical technologies such as solid oxide fuel cells, sensors or ceramic membranes for oxygen separation or partial oxidation of hydrocarbons. Usually, materials design is based on the partial substitution of a host cation for a different valence dopant, in order to increase the concentration of ionic or electronic defects via charge compensation mechanisms. However, as defects concentration increases, they will tend to associate and order, leading to extended and complex entities. Phase transitions are also a likely cause for formation of extended defects, such as phase or anti-phase twin boundaries. These extended defects demand for considerably energy to be disaggregated and their contribution to ionic conductivity is traditionally considered as negligible, or even null.

We have reported,[1,2] for a calcium titanate-based mixed conductor, $CaTi_{0.8}Fe_{0.2}O_{3-\delta}$, that the control of extended defects microstructure may lead to non-negligible gains in oxygen ionic conductivity resulting from additional paths for fast oxygen ion transport, as summarised in Fig. 1. By using different processing conditions, the formation of structural nanodomains was induced onto the orthorhombic structure which is sensitive to oxygen stoichiometry. The materials with such complex microstructure evidenced significant gains in oxygen ionic conductivity that were attributed to fast oxygen diffusion along domain boundaries. These domains result from the formation of planes of ordered FeO_4 tetrahedra that intercept along planes forming domain boundaries. Further atomistic simulations studies revealed that domain boundaries are preferential sites to accommodate oxygen excess, or Fe^{4+}, thus playing a major role on the defect microstructure and oxygen diffusion.[3]

This work demonstrated that extended defects may play an important, somewhat unexpected role on the development of electrochemically active materials for high temperature applications. The knowledge and the possibility to engineer these complex microstructures are fundamental to address their potential. The application of domain engineering aiming to improve the high temperature transport and electrochemical properties offers new and exciting possibilities as recently suggested when transforming an extended defect system based on La-substituted $SrTiO_3$ and then changing the composition to disorder these defects and create new electrochemically active materials for use in solid oxide fuel cells.[4] Additional evidence for the relevance of extended defects, in particular twin boundaries [5,6], to ionic transport are now starting to appear in the literature. These findings are certainly of major importance to the fields of ceramics, solid state ionics and solid state chemistry and physics.

Collaborators of this work: J.C. Waerenborgh (Sacavém), V.V. Kharton (Aveiro), G.M. Mather (Madrid).

Filipe Figueiredo (born 1970) graduated in Ceramics and Glass Engineering (1993) from the University of Aveiro and obtained a PhD from the same University in 1999 working on to explore the potential of novel composite mixed conducting materials for application as cathodes in Solid oxide fuel cells. After the PhD, he joined the Open University in Lisbon where he keeps a position as Auxiliary Professor. After several years of collaboration with Aveiro, he becomes a member of CICECO in 2004. His research interests are focused on the synthesis, processing and study of relationships between structure, microstructure and electrical and electrochemical properties of ceramic materials for high temperature electrochemical applications. He has contributed to about 60 papers in international refereed journals, with a citation record corresponding to *h* index 15.

Jorge Frade (born 1954) is Full Professor of Materials Science and Engineering. He obtained a PhD degree (1983) from the Department of Sheffield, UK. His main research interests are in the area of materials for fuel cells and other energy conversion systems. Other interests are related to modelling of solid state reactions, with emphasis on variable temperature. He has authored about 200 papers in international journals and received the FCT prize for Scientific Excellence (2004). Over the last 2 decades, his research group studied the ionic and electronic transport, electrocatalytic activity and other relevant properties of a wide variety of ceramic and composite materials for energy conversion, focused on compositional, structural, microstructural and phase stability factors. This research has been mainly supported by a wide range of international

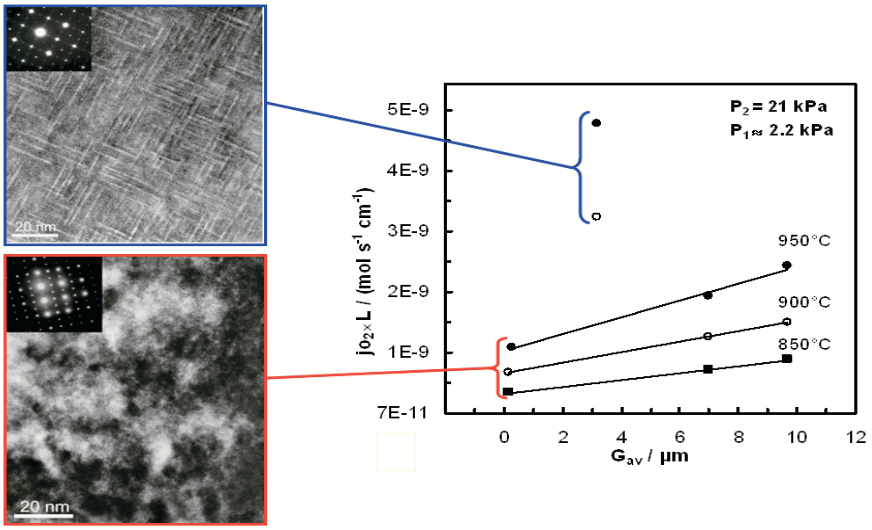

Figure 1. The plot shows oxygen permeation values obtained for $CaTi_{0.8}Fe_{0.2}O_{3-d}$ ceramics with different microstructure and grain size. The bottom micrograph shows a typical, fairly homogenous microstructure observed in ceramics. The blue circled image shows a fairly different microstructure consisting of microdomains. The oxygen flux, which is determined by the oxygen ion conductivity, is considerably higher for the latter samples with complex domain microstructure.

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Self-Healing Corrosion Protective Coatings With Nanoreservoirs of Corrosion Inhibitors

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We have developped novel protective systems with self-healing ability, composed of hybrid sol-gel films doped with nanocontainers that 'intelligently' release entrapped corrosion inhibitor. The nanoreservoirs store the active species preventing their interaction with the components of the coatings and liberate the inhibitor on demand when corrosion begins. The 'smart' inhibitor delivery is achieved since the rate of inhibitor release is controlled by external stimuli arising when a defect forms in the coating and corrosion starts (Fig. 1). This pioneer work is a breakthrough in the current corrosion protection technologies, increasing the service life of metallic structures. The creation of multifunctional coatings combining nanocontainers of different functional agents is the challenge for future investigations.

Active (corrosion inhibitors) and passive (barrier coatings) approaches are currently used for corrosion protection. Only the combination of both approaches affords reliable long-term protection of metallic structures which are in contact with electrolytes or humid environments.

Corrosion inhibitors may be introduced in the different components of the coating system: pre-treatment, primer and top coat. Inhibiting agents are effective only if their solubility in the corrosive environment is in the right range. Very low amount of inhibitor leads to lack of active agent at the metal interface and to weak inhibition. If the inhibitor dissolution is too high the substrate is protected for only a relatively short time since the inhibitor is rapidly leached out from the coating. Another possible drawback, is the inhibitor interaction with components of the coating resulting in the deactivation of the inhibitor and the degradation of the coating stability. The corrosion protection problem becomes more acute due to the restriction of the use of chromates, the most effective inhibitors known but strongly carcinogenic. The development of new approachs to introduce environmentally-friendly corrosion inhibitors, which may provide prolonged and 'smart' release of the inhibiting species on demand, is important for many industries where an adequate corrosion protection is needed.[1]

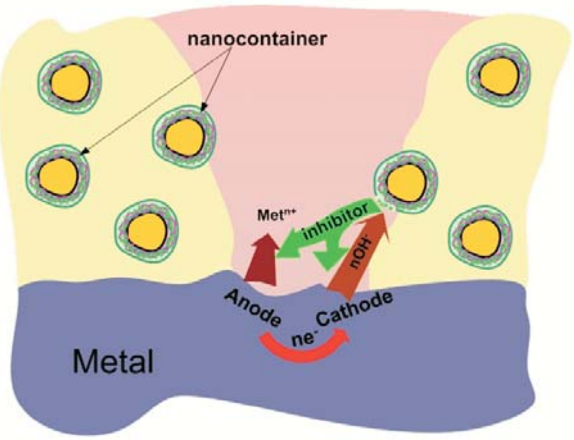

Figure 1. Scheme of the controllable release of the inhibitor from the nanocontainers and the 'smart' self-healing process.

Mário G. S. Ferreira is Full Professor at the Department of Ceramics and Glass Engineering, University of Aveiro. He obtained a first degree in Chemical Engineering from Instituto Superior Técnico in 1971 and his PhD in Corrosion Science and Engineering from UMIST, Manchester in 1981. His main scientific interests are focused on the study of Materials Degradation, Development of Advanced Materials and Ecological Processes for Surface Treatments.

Mikhail Zheludkevich is a post-doctoral researcher in the Department of Ceramics and Glass Engineering, University of Aveiro. He graduated from Belarusian State University in 1998 and in 2002 received his PhD in physical chemistry at the same University. He was part-time assistant professor in the University of Aveiro teaching corrosion science. His current interests include investigation of nanostructured sol–gel coatings doped with nanoreservoirs of corrosion inhibitors for intelligent storage/release properties.

We have developped different approaches of organic and inorganic inhibitor nanoencapsulation. The simplest nanoreservoirs are based on oxide nanoparticles doped with organic or inorganic inhibiting species,[2] or on nanoporous sublayers deposited on the metal surface and doped by the inhibitor.[3] A TiO$_x$ porous layer obtained by templating synthesis was used as nanostructured reservoir for an organic corrosion inhibitor. The reservoir consists of self-assembled titania nanoparticles forming a cellular network that replicates the surface structure of the etched alloy (Fig. 2). The nanoreservoir layer was coated with a sol-gel based thin hybrid film to provide an additional barrier. The nanostructured porous character of the titania layer provides a very high effective surface area for the adsorption of the inhibitor. The nanoreservoir approach avoids negative effects of the inhibitor on the stability of the sol-gel matrix and improves the release of the inhibitor in the places where defects develop. The novel coating system shows self-healing ability and enhanced corrosion protection when compared with undoped sol-gel films, or films doped directly introducing inhibitor in the sol-gel matrix.

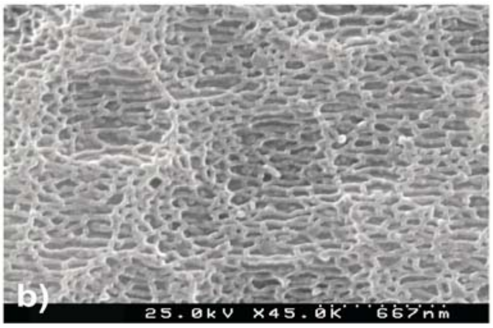

Figure 2. Micrograph of etched aluminium alloy coated with nanoporous TiO$_x$ layer.

More complicated nanostructures constructed by the core-shell Layer-by-Layer assembly of polyelectrolyte layers were also used for the inhibitors nanoencapsulation.[4] We used deposition LbL technology of oppositely charged polyelectrolyte molecules from solution to prepare reservoirs with regulated storage/release properties assembled with nanometer thickness precision. The nanoreservoirs were incorporated into the protective hybrid sol-gel coating (Fig. 3).

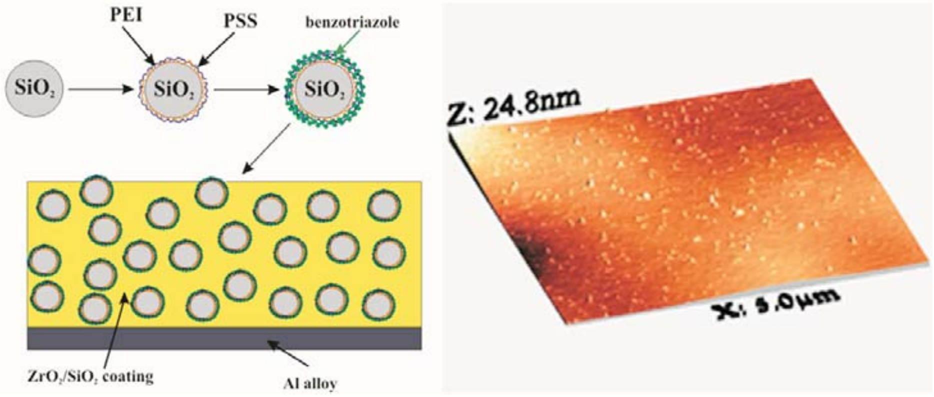

Figure 3. Left: schematic representation of the fabrication of composite hybrid coating loaded with benzotriazole nanoreservoirs. Right: AFM topography of the resulting sol-gel coating containing nanoreservoirs.

The scanning vibrating electrode technique (SVET) was employed to prove the self-healing ability of nanocomposite pre-treatments. This method shows the localized corrosion activity, mapping the distribution of cathodic and anodic currents along the surface. The Al alloy coated with undoped sol-gel film shows corrosion activity growing with time in the defect zone (Fig. 4). The sample coated with hybrid film doped with nanocontainers behaves differently. In the first 10 hours there are no remarkable currents in the defect zone. Only after *ca.* 24 hours the cathodic current appears. However, 2 hours after the activity started the corrosion is suppressed, decreasing the local current density. Cathodic activity in the defects becomes almost invisible after 48 hours of continuous immersion. This suppression of corrosion at a relatively large artificial defect formed in the coating system clearly shows the 'smart' self-healing ability of hybrid pre-treatments doped with nanocontainers.

Thus, the LbL assembled nanoreservoirs in the hybrid matrix release the inhibitor on demand healing the defects in the coating and providing an active corrosion protection with direct feedback. The latter is provided by the pH increase in the surrounding media of the nanoreservoirs due to started corrosion. Increased pH leads to the distortion of the polyelectrolyte layer structure and decomposition of PSS/benzotriazole complex provoking the release of benzotriazole from nanocontainers around the defect. The latter forms a thin adsorption layer on the damaged metallic surface hindering the anodic and cathodic corrosion processes and passivating the alloy.

The use of LbL polyelectrolyte layers in anticorrosion coatings opens a fresh opportunity to create cost-effective 'intelligent' corrosion protection systems with active feedback to the corrosion processes, possessing defects self-repairing action, presenting great potential for commercialization by producers of anti-corrosion pigments and coating formulators.

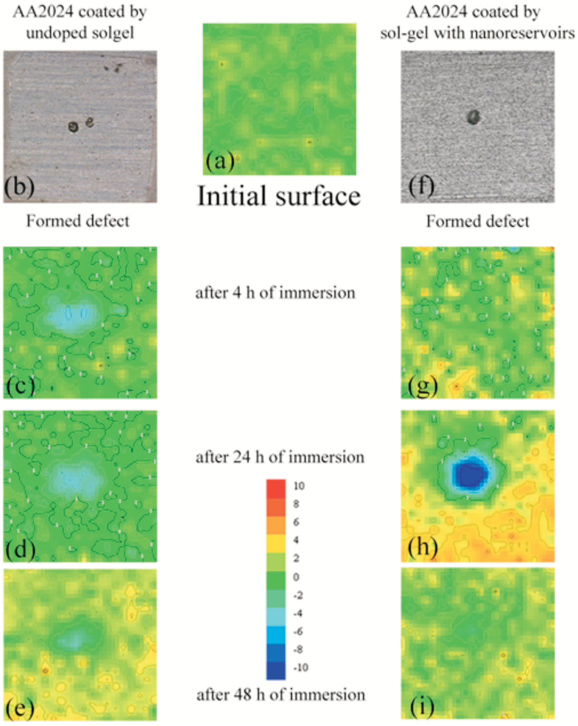

Figure 4. SVET maps of the ionic currents measured above the surface of the AA2024 coated with undoped sol-gel pre-treatment (a,c,d,e) and with pre-treatments impregnated by nanocontainers (g,h,i). Scale units: m Acm^{-2}. Scanned area: 2 mm × 2 mm.

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Organic-Inorganic Porous Materials

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The interest in organically functionalised mesoporous silicas is due to the potential utility of these materials in diverse fields, such as electric and optoelectronic devices, chemical sensors and catalysts. In 1992, the use of liquid-crystal templating initiated the research into the field of MCM-41 mesoporous silica. As a consequence of the single-size channels with tunable diameters, these materials have been used to host a variety of guests by means of post-synthesis derivatisation. This method often led to a quite low loading, an inhomogeneous distribution of the functional groups, and a decrease of the of pore volume.

To solve this problem, periodic mesoporous organosilicas (PMOs) started to be developed since 1999. The PMOs are prepared in one step synthesis by introduction of the appropriate organosiloxane precursor in the reaction medium.

Due to this new approach, the functional organic group resides inside of the walls as an integral part of the inorganic-oxide framework and the inorganic and organic moieties are covalently bounded to each other. In 2002, Shinji Inagaki, leader of the Frontier Research Group at Toyota Central R&D Laboratories, reported [*Nature*, 416, 304 (2002)] the synthesis and characterisation of a very revolutionary new mesoporous material (Fig. 1) containing pore walls completely regular, composed of orderly layers of benzene rings linked to alternating layers of silicate chains. The benzene rings can be functionalised, opening the door to a broad number of organic reactions that can lead to specially tailored properties, controlling chemicaland physical properties in the pores and in the framework at the same time. The same author claimed to Chemical & Engineering News that 'The result will impact a wide range of research fields--not only catalysis and adsorption, but also electrical, magnetic, and optical devices.'

A similar methodology can also be applied to modified natural layered clays in order to prepared functional porous clays heterostructures (PCHs).

We have prepared several functional mesoporous and clays organic-inorganic porous materials with tailored pore structure, framework composition and morphology. This was achieved by one-step pot synthesis, using the appropriate organosiloxane precursor and a template-directing agent. The high surface area materials with well-defined properties and with active metal species were tested as catalyst and as gases as adsorbent of volatile organic compounds.

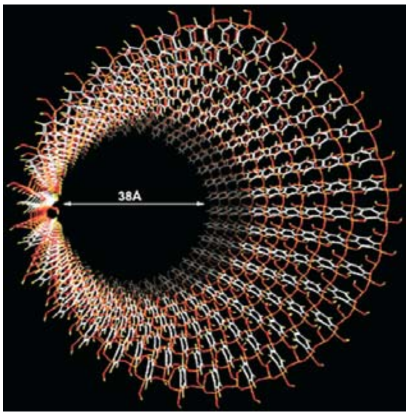

Figure 1. Mesoporous benzene-silica model [adapted from Nature, 416, 304 (2002)].

Paula Ferreira is a researcher at CICECO since December 2004. Since completing her PhD at the University of Aveiro in 2000, she was an Alexander von Humboldt Fellow at the Technical University of Munich and she worked as Assistant Professor at the Chemistry and Biochemistry Department of the Faculty of Sciences, University of Lisbon. Her research interests are in the synthesis, characterization and potential application of microporous and mesoporous organic-inorganic materials. Currently, she is working on the hydrothermal synthesis of mesoporous and 1-D nanostructures of perovskite-type materials for ferroelectric applications. She has more than 30 papers in scientific journals of SCI and she is involved as team leader in two R&D projects.

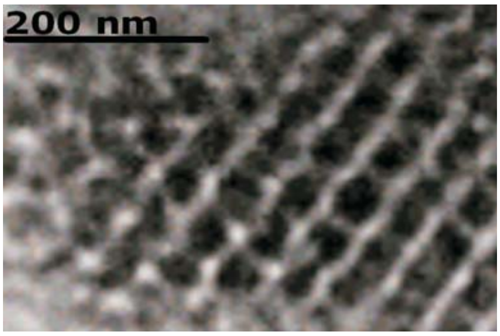

Figure 2. HRTEM image of surfactant free C_{18}-PMO.

The synthesis of periodic mesoporous benzene–silica hybrid materials exhibiting meso- and molecular-scale periodicity has been accomplished using surfactant templates with different alkyl-chain lengths (Fig. 2). The resulting materials possess similar lattices but different pore sizes. The benzene groups are preserved in the walls up to 550 ºC.

The same 1,4-bis(triethoxysilyl)benzene (BTEB) precursor was used on the synthesis of porous clay heterostructure. In the first step of the synthesis, the clay is expanded by ion-exchange of the interlayer cations with a cationic surfactant, to allow an easier access to the interlayer region. The air-dried ion-exchanged clay was then stirred overnight with a mixture of 1:1 of TEOS (Aldrich, 98%) and BTEB in the presence of a neutral amine as co-surfactant.

The surfactant template was extracted using a solution of 4.5 g of 37% HCl in 125 ml ethanol. The obtained benzene-silica hybrid clay has a specific surface area of more than 500 m^2/g and total pore volume near 0.4 cm^3/g. Due to its high adsorption capacity for different families of organic vapours such as selected volatile organic compounds such as methanol, methyl ethyl ketone, toluene and trichloroethylene, high hydrophobicity and thermal stability, the prepared material has potential application in VOC abatement and recovery. With the aim of preparing a hybrid material with an organic ligand with ability to metal coordinate, new organic inorganic hybrid mesoporous MCM-41 type materials have been synthesised by co-condensation different amounts of tetraethyl orthosilicate (TEOS) and 1,4 diazobutadiene (DAB) ligand RN=C(Ph)-C(Ph)=NR where R=$(CH_2)_3Si(OEt)_3$, in the presence of cetyltrimethylammonium bromide as the structure-directing agent (Figure 3). Surfactant extraction using acidified methanol leaves a hybrid mesoporous material with periodical hexagonal channels, large pore volume and high specific surface area. The introduction of a large amount, such as 20%, of organic building block decreases the order of the material and reduces the space available within the pore.

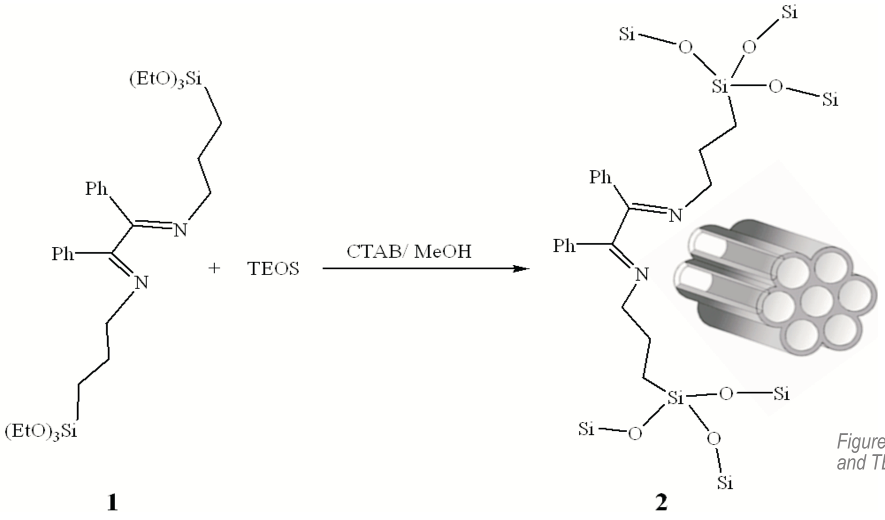

Figure 3. Scheme of the co-condensation of DAB type ligand and TEOS.

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Microwave Dielectrics and Lead-Free Relaxor Ceramics Based on Complex Titanate Perovskites

Wireless telecommunications are related to the sector of electronic industry showing the more dramatic growth in the last two decades. The use of ceramic materials in the modern high-frequency applications (resonators and filters) has stimulated the search for new compositions possessing the desired dielectric properties. There are three key properties that characterize high-performance dielectric resonators: a high dielectric permittivity, a low loss and a near-zero coefficient of the resonant frequency. These fundamental parameters, however, are inter-related, and so high dielectric constant dielectrics have strong temperature dependence of the permittivity. Polycrystalline ferroelectrics are known to exhibit very high permittivity. However, these cannot be considered as a promising microwave material because of their excessively high dielectric losses as well as a strong temperature dependence of the permittivity. Nevertheless, some ferroelectrics can be used as a component of solid solutions based on low-loss microwave dielectrics in order to increase the permittivity and to compensate for its temperature variation.[1,2] Moreover, in the last decade the intensive development efforts are being made in the direction of potential usefulness of ferroelectric materials in tunable microwave devices (high-frequency phase shifters, tunable capacitors, resonators and filters). High tunability (dependence of permittivity on applied field) of ferroelectric entities integrated into low-loss dielectric matrix opens up new possibilities of variation in selectivity and filtering of high-frequency signal. In this sense oxide perovskite materials give good opportunities, since (i) the perovskite-related family represents both ferroelectrically active and low-loss microwave dielectric materials, and (ii) their value of linear thermal expansion coefficient does not vary significantly with composition and structure, hence the problem of thermal misfit between adjoined active element and matrix is solved. Moreover, due to the ability of perovskites to form solid solutions in a wide range of substituting atoms one can control their dielectric properties by varying the chemical composition.

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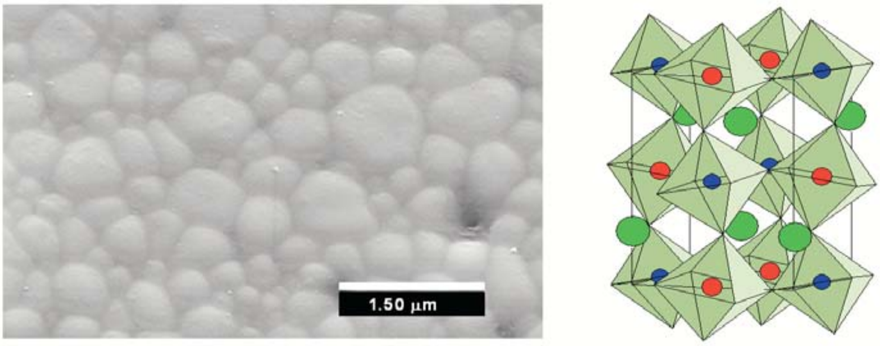

Figure 1. Left: SEM photographs of polished and thermal etched surface of the chemically prepared $La(Mg_{1/2}Ti_{1/2})O_3$ (LMT) ceramic.[1] right: The schematic representation of the two-tilted crystal structure of the LMT perovskite (right)

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Crystal structure and grain boundary engineering

A series of the perovskite solid-solution systems based on the low-loss dielectric lanthanum magnesium titanate (LMT) were systematically investigated with respect to their both crystal structure and dielectric characteristics. A non-conventional chemical method based on the Pechini route has been optimized and adopted for processing dense, homogeneous and fine-grain ceramics in those systems.

Multifunctional (ferroelectric-relaxor - microwave dielectric) perovskite solid solutions

In the ceramic compositions based on barium titanate (BT) doped with LMT, the continuous crossover from ferroelectric to relaxor behaviour has been observed.[4] This system has been explored in respect to a possible application of its compositions as tunable ferroelectric components in microwave devices.

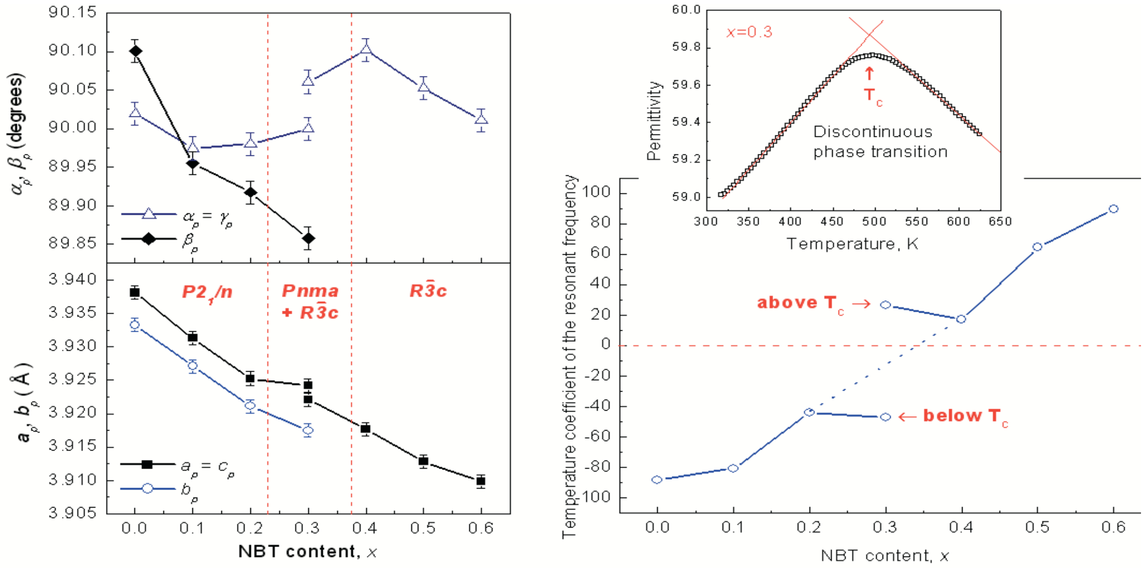

Figure 2. Left: Primitive perovskite unit-cell parameters (a_p, b_p, c_p and α_p, β_p, γ_p) as a function of composition x in the (1-x)LMT-x($Na_{1/2}Bi_{1/2}$)TiO_3 (NBT) system. Right: Temperature coefficient of the resonant frequency for (1-x)LMT-xNBT). inset: Temperature dependences of relative permittivity for the composition x=0.3 measured at 1 MHz.[3]

Crystal structure-dielectric properties relations

Sequences of structure transformations as functions of composition and temperature were revealed. It has been found that a character of variations of dielectric permittivity and temperature coefficient of the resonant frequency in non-ferroelectric perovskite ceramics is determined by a type of the phase transition (continuous or discontinuous) between their crystal structure modifications.

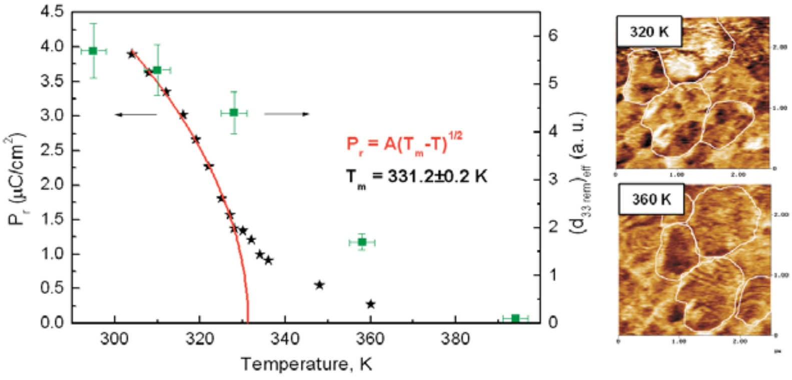

Figure 3. Right: Remnant polarization (P_r) and remnant $(d_{33})_{eff}$ coefficient as a function of temperature in ceramic $BaTiO_3$ doped with 2.5 mol% LMT. P_r is fitted by the relation $P_r \sim (T_m - T)^{1/2}$ (solid line). Left: Piezoresponse force microscopy (PFM) images of the BT:2.5%LMT ceramics measured below and above the transition temperature.[5]

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Cellulose: a Never-Ending Source of Remarkable Functional Materials

Cellulose is the most abundant natural polymer on earth and nature displays its supramolecular structure in a remarkable variety of visible and palpable morphologies. From its very inception, humanity has taken full advantage of these manifestations, first for shelter and clothing, then for making progressively more sophisticated artefacts, of which paper is the highest symbol.

In spite of the relentless efforts devoted to the exploitation of this renewable resource throughout the ages, and of notable recent advances in numerous domains, there is still plenty of scope for novel materials to be created and our group has been, and continues to be, involved in this quest.

Cellulose fibres, ubiquitous in our planet, albeit in different shapes and from different species, possess outstanding properties in terms of mechanical strength, chemical behaviour, etc. which make them entirely suitable for original applications, such as (i) reinforcing elements in composite materials, (ii) paper-based artefacts with specific surface properties and (iii) sources of single-component composites.

Within its wider strategy, aimed at searching for new value-added functional materials based on renewable resources, our group has been engaged in these three research avenues and has produced some very stimulating results.

With respect to the first topic above, our search has focused on the selective transformation of the surface hydroxyl groups into non-polar moieties capable of creating a highly compatible interface with conventional polymer matrices like polyethylene and polypropylene. Thus, composite materials can be prepared in which glass fibres, the conventional reinforcing elements, are replaced by cellulose counterparts, with the basic advantages, among others, of the possibility of recycling (as imposed by recent legislation), coupled with a substantial weight gain (fundamental in energy saving associated with vehicle applications) and, of course, the exploitation of a ubiquitous cheap renewable resource. The study of the surface modification of cellulose fibres with fatty acids represents a typical example of our application of this approach.[1]

With respect to the second topic, one of our aims was to generate superhydrophobic surfaces and this was achieved by the use of reagents bearing perfluoro moieties. Both reversible and permanent superhydrophobic features (Fig. 1) were attained as a function of the specific nature of the reagent and this opens the way to different applications in papermaking, packaging, etc.[2]

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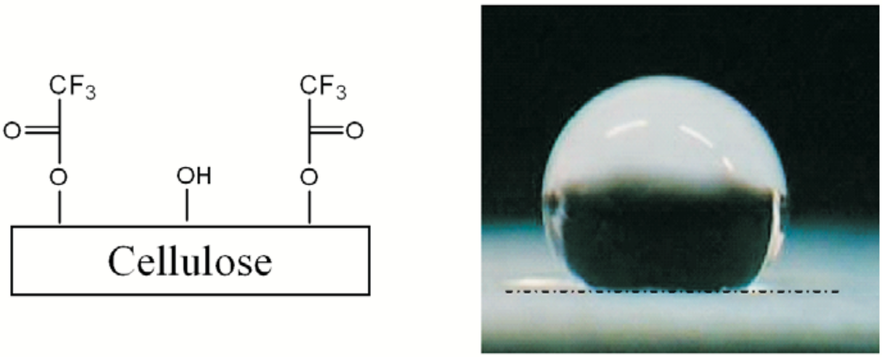

Figure 1. The shape of a water droplet deposited onto cellulose fibres modified at their surface with trifluoroacetic anhydride.[2]

Finally, with respect to the third topic, we explored the novel idea of modifying these fibres by a controlled in-depth chemical reaction, viz. a different strategy compared with topic (i), whereby the modification was applied in a controlled fashion so as to reach a predetermined depth, thus modifying part of the fibre thickness and not only its outer regions. As an example, the use of fatty acids, i.e. reagents also derived from renewable resources, for the in-depth esterification of the cellulose hydroxyl groups, gave rise to fibres maintaining their inner crystalline core, but displaying a thermoplastic character associated with their modified sleeves. The hot pressing of these partly esterified filaments induced their merging to form a continuous film in which the ensuing cellulose ester matrix was reinforced by the pristine inner body of the crystalline fibres. A composite material was therefore generated and processed from cellulose fibres as its only precursor. Figure 2 illustrates the morphology of one such peculiar composite material, in which both the thermoplastic matrix (modified cellulose) and the reinforcing fibrous elements (unmodified crystalline fibre inner core) are clearly displayed.

This work is done in collaboration with Professors Carlos Pascoal Neto and Armando J. D. Silvestre.

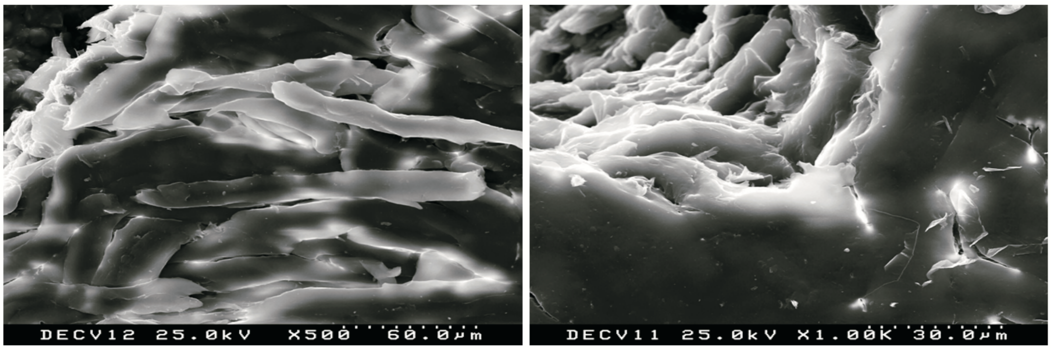

Figure 2. SEM images of cellulose fibres modified in depth with fatty acyl chlorides.

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Rapid Metabolic Assessment in Fluids and Tissues

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The key idea of this work is that many different metabolites may be detected and quantified simultaneously, in the liquid (biological fluids or extracts) or solid state (biological tissues). The technology used is High Resolution NMR, with the use of Magic Angle Spinning (MAS) for the analysis of solid samples. The tandem use of chemometrics enables interpretation and validation of the spectral profiles of complex liquid and solid mixtures.

The strength of the NMR/Chemometrics strategy is the "detection of the unexpected". This means that it allows for the detection of metabolite changes of which there was no prior knowledge. In this way, truly new incursions may be made in new grounds of metabolism and metabolism perturbations e.g. disease or disorders, nutritional effects, toxicological effects of drugs or natural products.

Metabonomics is the new term that relates to the simultaneous monitoring of many metabolites in order to detect the effects of different system perturbations. NMR is not the only technique that enables this, however, and in spite of its low sensitivity, it offers advantages such as non-invasiveness in the analysis of liquid and solid whole samples, with little or no sample preparation.

Our first example regards the use of NMR/Chemometrics for the characterization of the glycogen storage disease (GSD), with the detection of an expected and unknown biomarker compound for the disease (-hydroxyisobutyrate). Figure 1 shows the result of a chemometrics study (using principal components analysis-PCA) of the 1D ^{1}H NMR spectra of the plasmas of GSD patients and controls, suggesting the possibility of using the NMR-based method to detect and evaluate the extent of the disease.

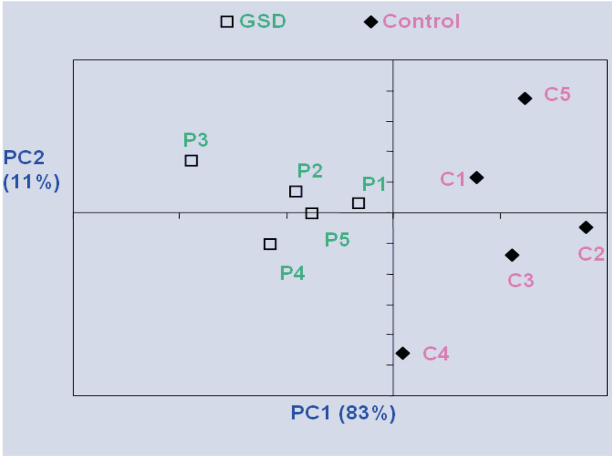

Figure 1. Scores plot for the PCA of 1D ^{1}H NMR spectra of the plasma of GSD patients (Pi) and controls (Ci).

Ana Gil is Associate Professor, University of Aveiro since 1998. She got her Ph.D. in Chemistry, University of East Anglia, U.K., in 1992. Her first degree in Chemistry was obtained in1987 at the University of Coimbra, Portugal (mark 17/20). Scientific interests: structural characterisation of purified cereal proteins for the understanding of their functional properties; structural studies of cork and other lignocellulosic materials; structural and dynamic studies of mono-, oligosaccharides and polysaccharides in the solid state; development of rheo-NMR techniques for the interpretation of rheological properties at the molecular level; development of spectroscopy-based methods for the routine quality control of products and processes in the food industry (brewing industry and beverages industry); analysis of human biofluids and biological tissues for the biochemical characterisation and early diagnosis of diseases; development of new biomaterials and their ex-vivo and in-vivo testing and evaluation for different uses. She has published 10 book chapters, 49 SCI papers, and presented 101 communications in scientific meetings.

The second example regards the application of MAS NMR to the metabolic evaluation of liver grafts i.e. biopsies used for transplant. Figure 2 shows the ^1H High Resolution (HR)-MAS NMR records of two complementary NMR experiments, each of which registers the signals of many metabolites simultaneously. The spectrum in Fig. 2a shows signals of both large and small compounds whereas Fig. 2b selects for the signals of small compounds alone. A comparative study for different liver grafts allowed a determination of their metabolic profiles to be made before removal from donors, during cold perfusion and after implantation into recipients. Results have shown biochemical differences between livers used for transplants that can be related to the degree and type of lipid composition which in turn might relate to donor organ quality.

Commercialization of the NMR/Chemometrics models is envisaged for application in rapid diagnostics of a range of metabolic problems and, at a shorter-term, for routine quantification of metabolites in biofluids or in mixtures of relevance for instance in the food industry.

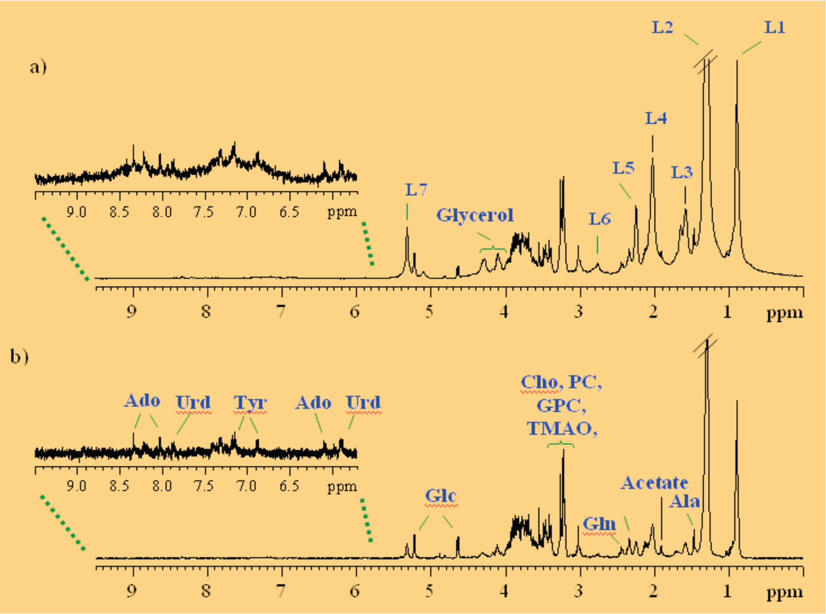

Figure 2. 400 MHz ^1H HR-MAS NMR spectra of a human liver biopsy sample (rotation rate 4 kHz): a) standard 1D spectrum, b) spin-echo (CPMG) spectrum (to view only small Mr compounds). L1, lipid $C\underline{H}_3$; L2, lipid $(C\underline{H}_2)n$; L3, lipid $C\underline{H}_2C\underline{H}_2CO$; L4, lipid $C\underline{H}_2$-CH=CH; L5, lipid $C\underline{H}_2CO$; L6, lipid CH=CH-$C\underline{H}_2$-CH=CH; L7, lipid $C\underline{H}$=$C\underline{H}$; Cho, choline; PC, phosphocholine; GPC, glycerophosphocholine; TMAO, trimethylamine-N-oxide; Bet, betaine; Glc, glucose; Val, valine; Leu, leucine; Ala, alanine; Gln, glutamine; Tyr, tyrosine; Urd, uridine; Ado, adenosine.

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The First Structure from the SOUL/HBP Family of Heme Binding Proteins: Murine P22HBP

Using Nuclear Magnetic Resonance (NMR) spectroscopy, the first 3D structure of a protein from the SOUL/HBP family of heme-binding proteins, murine p22HBP, has been determined. Results from titrations of p22HBP with heme have allowed the novel tetrapyrrole binding site to be located and the mode of binding identified. This is the first time this type of fold has been seen in a non-bacterial organism.

Hemes are one of the most visible and versatile class of cofactors utilized in biology. Heme in hemeproteins is involved in many aspects of oxidative metabolism including oxygen transport by hemoglobin and storage by myoglobin, electron transfer by cytochromes, generation of cellular energy in the respiratory chain and detoxification by enzymes such as P450 and peroxidases. In mammals heme synthesis (Fig. 1) occurs mainly in developing erythroid cells (~85%), hepatocytes and muscle cells (for myoglobin), although heme is synthesized in virtually all tissues.

The p22 Heme Binding Protein (p22HBP) is a cytosolic protein expressed in liver, spleen and kidney cells. No function is known for this protein except that it binds porphyrins, hemin in particular, with very high affinity. This had led people to suggest that, as porphyrins and metallated porphyrins (e.g., heme) are extremely reactive and poorly soluble in aqueous solution under physiological conditions, p22HBP may be one of a number of intracellular heme binding proteins that act as a buffer during induced heme synthesis (figure 1). We decided to determine the 3D structure of p22HBP, in order to gain insights into the function of the protein and the way in which it binds heme.

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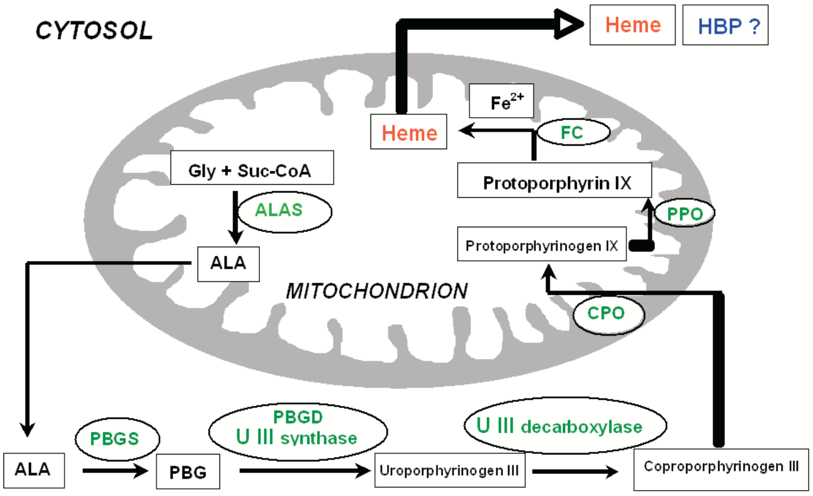

Figure 1. Schematic diagram of heme biosynthesis

Brian J Goodfellow is a member of staff at the University of Aveiro since 1998 and his research in CICECO involves in a number of projects all of which involve NMR spectroscopy: NMR of Proteins; Application of NMR to Biofluids; Spectroscopy of Biomaterials; Development of new NMR methods; Inorganic complexes containing Ru.

NMR spectroscopy and X-ray crystallography are the only methods available to determine the 3D structure of proteins. In order to obtain a 3D structure by NMR the protein must be purified, isotopically labeled (the natural ^{14}N and ^{12}C atoms are replaced by ^{15}N and ^{13}C atoms) and available in large quantities. This is achieved using molecular biological techniques and involves cloning and over expression. Once the protein is available in a pure labeled form NMR spectra can be obtained. In protein NMR we observe hydrogen nuclei (protons) and as a protein has thousands of protons a large number of signals are observed. As overlap always occurs NMR experiments involving 2-dimensional and 3-dimensional spectra have to be used. This is a time consuming process and a 3D NMR spectra may take up to 2 days to record. To determine a structure a number of different 3D spectra (each giving different information) are recorded. The initial analysis involves identifying every signal in the spectra and the corresponding proton which gives rise to that signal. After identifying the signals from each proton a spectrum that utilizes the Nuclear Overhauser Effect (NOE) is analyzed. This spectrum has information about distances between protons in our protein. Using a combination of the chemical information available via the primary sequence of the protein, and the experimental distances from NOE spectra, allows a 3D structure to be obtained. This process was carried out (in collaboration with the University of South Florida, the Medical College of Wisconsin and the New University of Lisbon, POCTI/BME/39184/2001) on mouse p22HBP labeled with ^{15}N, ^{13}C and ^{2}H and resulted in the first 3D structure of a protein from this particular family (Fig. 2). This was also the first time this type of fold had been seen a non-bacterial organism.

By titrating the protein with heme and observing the effect on the signals of the protein we were able to identify the binding site (Fig. 3). This site was found to coincide with an hydrophobic patch on the surface of the protein allowing us to conclude that a hydrophobic interaction rather than any direct binding explains the affinity of heme for p22HBP (Fig. 4).

Future work now involves determining the function of p22HBP, and/or tailoring the properties of p22HBP (modifying residues at the binding site) to allow it to be used as a heme sensor, or as a heme transport system. Chemical modification of the protein may also allow the protein to be tethered to a surface and used in functional biomaterials.

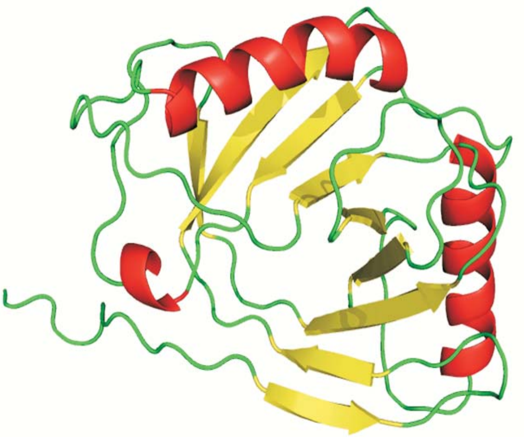

Figure 2. The NMR solution structure of murine p22HBP. The alpha-helices and beta-sheet sections are shown in red and yellow respectively (PDB 2GOV).

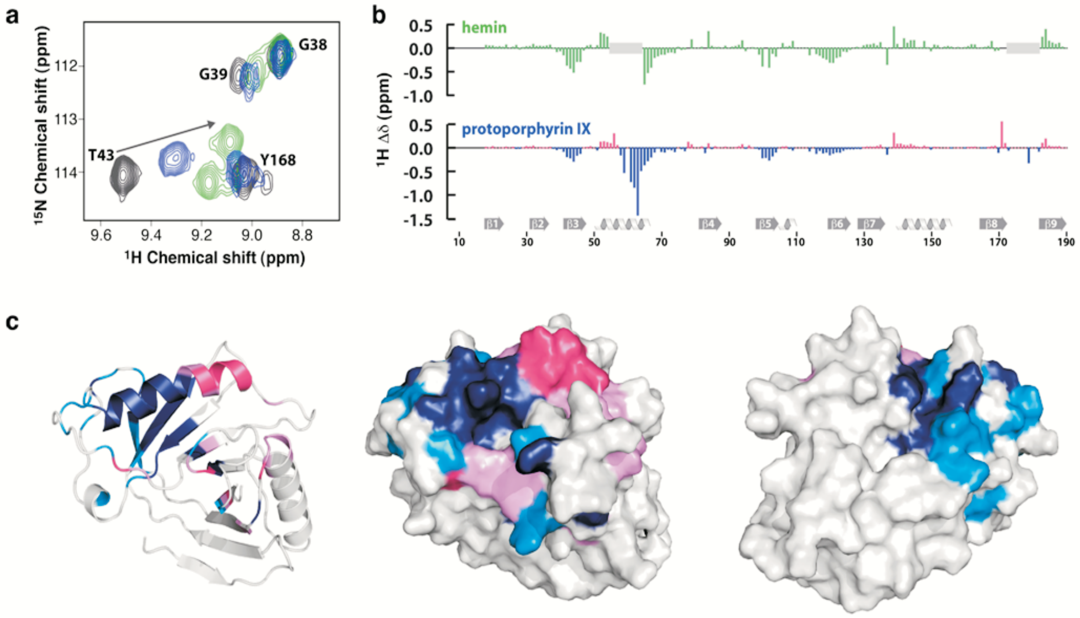

Figure 3. NMR titrations show that HBP binds heme and PPIX. (a) Overlay of a small region of the TROSY spectra for p22HBP (black contours), p22HBP-PPIX (blue contours) and p22HBP-hemin (green contours) showing shift perturbations upon tetrapyrrole binding. (b) Experimental chemical shift differences observed for murine p22HBP upon binding of hemin and PPIX. (c) PPIX-induced shift perturbations displayed on the p22HBP structure. Small, negative shifts are shown in cyan, large negative shifts in blue, small, positive shifts in violet, and large positive shifts in magenta. Ribbon (left) and surface (center) representations are shown in the same orientation, as well as a view of the surface rotated 180º about the vertical axis (right).

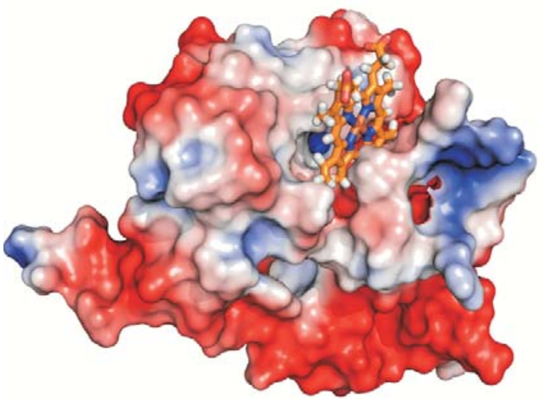

Figure 4. The p22HBP structure with hemin docked at the binding site based on PPIX-induced ring current shifts. The site corresponds to a hydrophobic cleft.

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Mixed Organometallic Oxoanion Polymers With Tailored Catalytic Properties

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Research on organic-inorganic hybrid materials with infinite (polymeric) structures has grown exponentially over the last ten years or so. One of the most appealing strategies is the formation of coordination networks through the aggregation via intermolecular bonds of two or more modular units. The self-assembly of organotin cationic fragments such as Me3Sn$^+$ with different anionic metal-containing species has provided a large family of supramolecular organometallic networks with either one-dimensional (1D), 2D or 3D architectures. Our work focuses on compounds containing metal oxoanions of the type MOx^{y-}. We began by studying the family of organotin metalates $[(R_3Sn)_2MO_4]$ (M = Mo or W), which are readily prepared from parent R3SnCl and $NaMO_4 \cdot 2H_2O$. $[(Me_3Sn)_2MoO_4]$ has a layered structure built up of tetrahedral MoO_4 and Me_3SnO_2 trigonal-bipyramids (with shared oxygen atoms, Fig. 1). Although these hybrids have many potential applications, particularly in the fields of optoelectronics, gas sorption and catalysis, most published work concentrates on the synthesis and characterization. We have made progress in using the materials as catalysts for the oxidation of organic compounds.

A series of organotin molybdates, $[(R_3Sn)_2MoO_4] \cdot nH_2O$ (R = methyl, n-butyl, cyclohexyl, phenyl and benzyl) were prepared and characterized in the solid state by powder X-ray diffraction, IR and Raman spectroscopy, MAS NMR (^{13}C and ^{119}Sn) and EXAFS.[2,3] Analysis of the Mo K-edge and Sn K-edge EXAFS data confirmed that the structures of all five compounds arise from the self-assembly of tetrahedral $[MoO_4]^{2-}$ sub-units and $[R_4Sn]^+$ spacers.

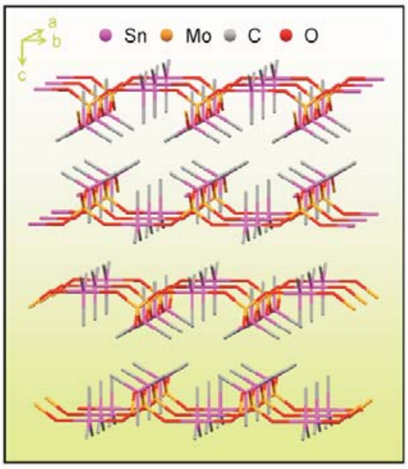

Figure 1. The layered structure of $[(Me3Sn)_2MoO4]$. H-atoms have been omitted for clarity

The organotin molybdates and the tungsten analogue $[(nBu_3Sn)_2WO_4]$ were tested as catalysts in the liquid-phase epoxidation of cyclooctene using aqueous hydrogen peroxide as the oxidant (Eq. 1 in Fig. 2).[2,4] Epoxides are

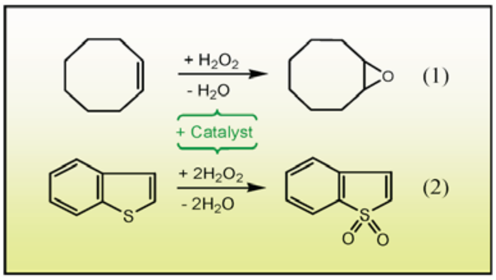

Figure 2. Two of the oxidation reactions studied in the present work

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valuable organic intermediates and their preparation using aqueous H_2O_2 is important from the perspective of 'green' chemistry. The catalytic results varied considerably according to the nature of the tin-bound R group. For R = *n*-butyl, the molybdate was generally found to be more active than the tungstate, although both compounds could be used as solid catalysts to give the desired epoxide in quantitative yield within 5 h at 55 ºC. Comparatively lower activities were obtained when tert-butyl hydroperoxide (TBHP) was used as the oxidant rather than H_2O_2, although the heterogeneous catalyst $[(nBu_3Sn)_2MoO_4]$ could be recycled without measurable loss of activity.

The organotin molybdates were also tested as catalysts for the oxidation of benzothiophene with aqueous H_2O_2 under mild conditions.[3] Benzothiophene is one of the refractory sulfides that has to be removed from liquid hydrocarbon fuels to reduce the sulfur content to ultra-low levels. The liquid oxidation process with H_2O_2 is a possible environmentally friendly alternative to existing catalytic hydrodesulfurization processes. In the catalytic reactions with the organotin molybdates, the 1,1-dioxide (sulfone) was the only observed product (Eq. 2 in Fig. 2). Under appropriate conditions, the tribenzyltin derivative could be used as a recyclable heterogeneous catalyst to produce the sulfone in quantitative yield within 24 hours.

We have also investigated the properties of the trimethyltin vanadate $[Me_3SnVO_3]$ [5]. The phase purity and structure of the as-synthesized microcrystalline compound was confirmed by carrying out a full Rietveld structural refinement from conventional powder X-ray diffraction data collected at ambient temperature. The structure consists of infinite metavanadate chains which are linked by Me_3Sn^+ cations (Fig. 3). A novel triethyltin vanadate has also been prepared and is currently the focus of a structural study. The trimethyltin derivative was applied as a catalyst for the liquid-phase epoxidation of olefins using TBHP as the oxidant. The reaction rate for the different substrates followed the order: cis-cyclooctene > (R)-(+)-limonene ~ trans-2-octene > cyclododecene > styrene > 1-octene; the corresponding epoxides were the only observed products. Leaching tests indicated that the catalytic epoxidation of cyclooctene was mainly heterogeneous in nature.

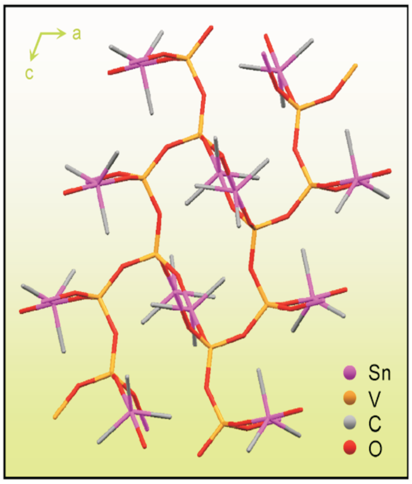

Figure 3. View along the b-axis of [Me3SnVO3]. H-atoms have been omitted for clarity

In summary, hybrid materials built from the combination of transition-metal oxoanions and organometallic cations have the potential to be important catalysts or co-catalysts for many chemical transformations. The nature of the tin-bound R group has a direct influence on the structure of the hybrid material and their catalytic properties. Our recent research has been directed towards the use of chiral organotin compounds for the preparation of hybrids that may function as enantioselective catalysts.

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‘There is Plenty of Room at the Bottom’ for Relaxor Ferroelectrics

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Relaxor ferroelectrics include a large group of solid solutions, mostly oxides, with a perovskite or tungsten bronze structure. In contrast to ordinary ferroelectrics (FE) whose properties are well explained and described over the 50 years of studying, relaxor ferroelectrics (RF) are the “enigma” of modern solid state physics and chemistry.[1] They possess a number of unique features such as broad dielectric maximum and its frequency relaxation, local symmetry differing from the macroscopic one, nonergodic “glassy” behavior at low temperatures etc. Very high piezoelectric and dielectric properties are observed in solid solutions between normal ferroelectrics and relaxors as exemplified by PZN-PT and PMN-PT single crystals. Unusually high properties make relaxors very attractive for a variety of applications. Most of the properties of ferroelectric relaxors were attested to the existence of so-called polar nanoregions (PNR) or nanodomains: small dynamic areas with correlated polarization, the size of which was estimated as 3-20 nm at room temperatures. As many useful properties originate from PNRs, it is of very high interest to study their behavior at the nanoscale, i.e., at the scale compatible with the modern Scanning Probe Microscopy (SPM). In CICECO, a method of studying relaxors by SPM was developed.[2] We have observed piezoelectric contrast on the surface of macroscopically nonpolar relaxors such as $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), $PbZn_{1/3}Nb_{2/3}O_3$ (PZN), $(Pb,La)(Zr,Ti)O_3$ (PLZT), and solid solutions based on them. The measure of polarization coherence, so-called correlation length could be directly derived from images (Fig. 1).

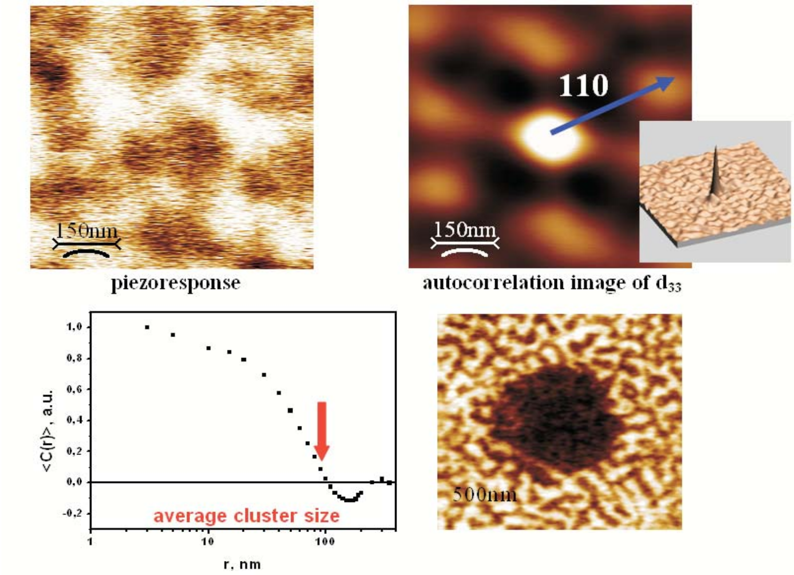

Figure 1. Typical piezoelectric contrast in PMN-PT single crystals and the definition of correlation length measurements in RF.[3] *The picture in lower right corner illustrates PFM-induced polar state.*

Andrei Kholkin is a principal investigator of CICECO. He is known for his studies of piezoelectric properties of ferroelectrics, degradation phenomena in ferroelectrics, piezoelectric MEMS, and scanning probe microscopy of ferroelectrics. He is the author or coauthor of about 200 technical papers in this area including several reviews and book chapters. He is currently a coordinator of two European projects in the field of ferroelectrics and serves as an Associate Editor for Transactions on Ultrasonics, Ferroelectrics and Frequency Control of IEEE. He is a member of the Ferroelectric Committee of IEEE since 1998 and was recently awarded by the Senior Member grade of this society. He was a recipient of the “Estimulo de Excellência” award of Portugal and is a member of Advisory Boards of several conferences on ferroelectrics and related materials.

The measurement revealed also that local RFFE phase transition can be induced by the application of the small voltage to the PFM tip.[4] As a result, the stable ferroelectric state was observed at the temperatures much higher than the freezing temperature of relaxors (Fig. 1).

The presence of PNRs was observed for the first time in materials with giant piezoelectric effect PZN-PT. The nature of d_{33} in excess of 2000 pm/V was attested to the nanoscale domains of 1-25 nm in size (Fig. 2).

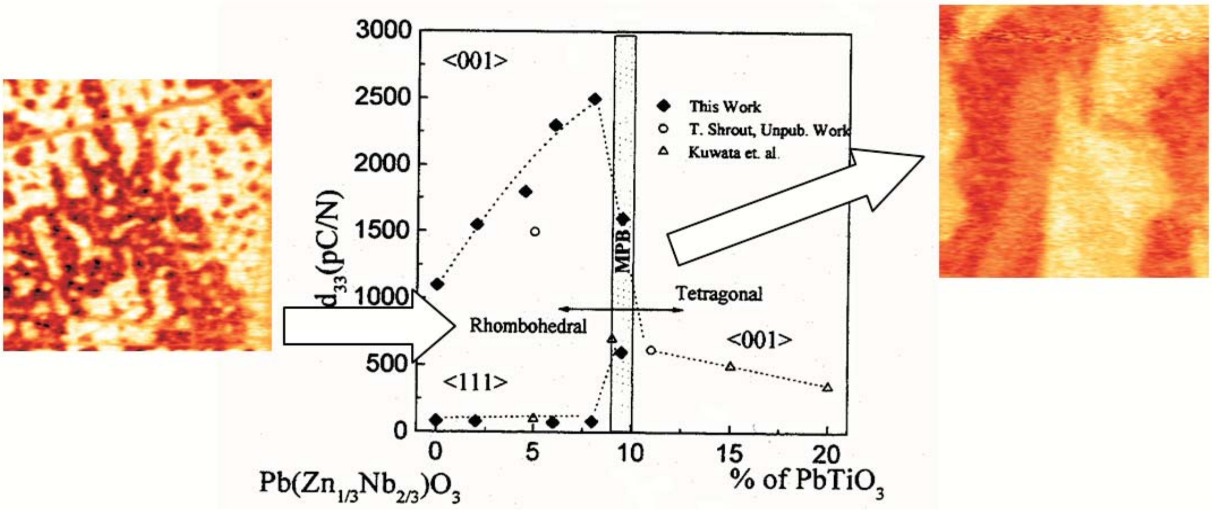

Figure 2. Polar nanostructures on the (001) surface of PZN-PT crystals responsible for giant piezoeffect for this cut. In comparison, low piezoelectric properties and no nanodomains are observed on (111) cut.[5]

The series of paper on the relaxor thin films revealed that relaxors are prone to a spontaneous RFFE phase transitions under the influence of la built-in electric field (self-polarization).[6] Such films look like a nanocomposite comprising relaxor and ferroelectric areas. In this way, the properties of relaxor films can be intentionally modified using self-assembly or nanopatterning methods thus making artificial nanostructures with controlled properties.

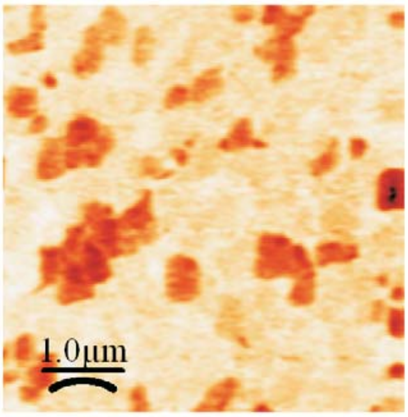

Figure 3. Topography (left) and piezoresponse (right) of the PMN-PT thin film prepared by laser ablation.[6]

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Multiferroic Composites: a New Approach to Multifunctional Materials

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The science and technology in the 21st century will rely heavily on the development of new materials and structures. Such materials should be innovative with regard to scale, structure, function, and design. Multifunctional materials are among the most promising directions of research and there exists a coordinated effort all over the world aimed at finding new solutions based on the advanced deposition and characterization tools. Multifunctional material is typically a composite or hybrid of several distinct phases with each phase executing a different function such as transport, sensing, actuating, etc. Among multifunctional materials, *multiferroics*, i.e., materials exhibiting a coexistence of *ferroelectric, ferromagnetic, and/or ferroelastic* responses, attract significant interest because of their potential applications including multi-sensors of magnetic/electric/elastic fields, microwave devices based on negative refractive index (metamaterials), combined piezoelectric/magnetic actuators and motors, multiple memory elements, to name just a few.[1]

One approach undertaken at CICECO [2] is to built a ceramic composite multiferroic material based on the intimate mixture of mutually interconnecting ferroelectric and ferromagnetic grains, where the mechanism of the magnetoelectric coupling could be due to either mechanical strain exerted via piezoelectric or magnetostrictive effects or field effect of ferroelectric phase that will modify the electronic and, subsequently, magnetic properties of a ferromagnetic or Fig. 1. SEM image of (La,Sr)MnO_3-$LuMnO_3$ antiferromagnetic material. This could be achieved via a simple mixed oxide method using an effect of immiscibility in solid solutions.[2]

The interaction level will depend on how fine are the interconnected grains and how clean are the grain boundaries and interfaces. An example of such composite based on x(La,Sr)MnO_3-(1-x)$LuMnO_3$ is shown on Fig. 1. Intimate mixture of the ferroelectric and ferromagnetic phases near the percolation threshold allows relatively high magnetoelectric and piezomagnetic effects to be achieved in such composites. The perfect phase separation is observed above the solubility level of about 2 % . Such artificial “metamaterials” are of primary importance for microwave applications and are now tested in the GHz frequency range.

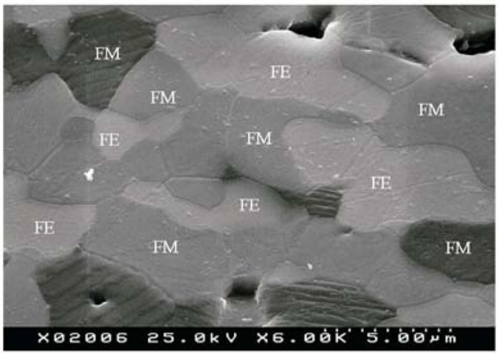

Figure 1. SEM image of (La,Sr)MnO3-LuMnO3.

Andrei Kholkin is a principal investigator of CICECO. He is known for his studies of piezoelectric properties of ferroelectrics, degradation phenomena in ferroelectrics, piezoelectric MEMS, and scanning probe microscopy of ferroelectrics. He is the author or coauthor of about 200 technical papers in this area including several reviews and book chapters. He is currently a coordinator of two European projects in the field of ferroelectrics and serves as an Associate Editor for Transactions on Ultrasonics, Ferroelectrics and Frequency Control of IEEE. He is a member of the Ferroelectric Committee of IEEE since 1998 and was recently awarded by the Senior Member grade of this society. He was a recipient of the “Estimulo de Excellência” award of Portugal and is a member of Advisory Boards of several conferences on ferroelectrics and related materials.

Another approach pursued at CICECO is to use Scanning Probe Microscopy (SPM) to observe mutual conversion of magnetic and electric variables by applying high electric field to the sharp SPM tip. This will allow direct conversion of the mechanical/magnetic/electric energy and will pave the wave for "universal" memory applications. Fig. 2 illustrates our recent findings on the electric field writing on LSMO-based single crystals with low Sr content where the material is in the insulating antiferromagnetic state.

In the initial state (Fig. 2a), no piezoelectric contrast is observed due to centrosymmetric structure of LSMO, but after the writing with the voltage +30 V a white stripe appears (Fig. 2b) due to the locally induced piezoelectric effect. The hysteresis observed by sweeping the applied bias field attests the material to the ferroelectric class signifying effective local Jan-Teller phase transition into the polar phase [3]. The existence of ferroelectricity was confirmed by the measurements of piezoresponse hysteresis (Fig. 3). The multiferroic work is performed under the auspices of FP6 STREP project "Multiceral" (NMP3-CT-2004-32616) which is coordinated by CICECO.

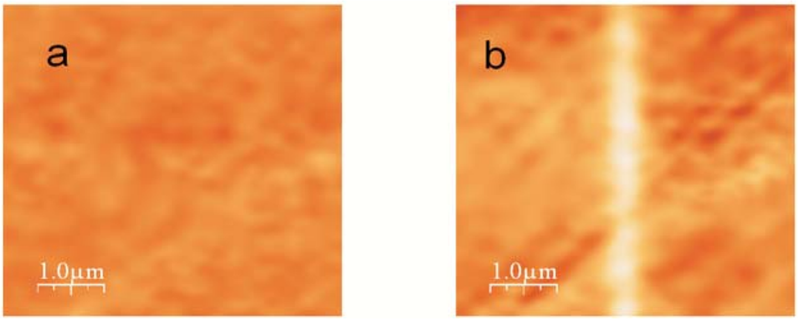

Figure 2. (a) PFM image (no poling), (b) electric-field-induced piezoresponse in (La,Sr)MnO3.

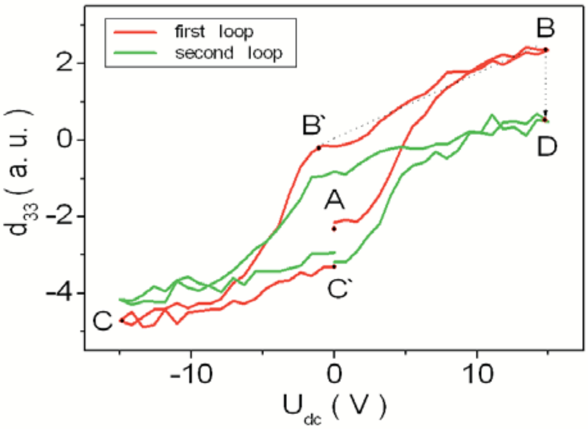

Figure 3. Piezoresponse hysteresis loop in centrosymmetric (La,Sr)MnO3 indicating locally induced feroelectricity.

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Wastes Recycling and New Materials

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Achieving sustainable development is now widely regarded as a key social, economic and technical driver, and a central consideration in assessing the value and quality of future developments. The volumes of materials consumed, the amounts of waste sent for disposal and the amount of energy used are key indicators of sustainability. However, the current massive growth in population, coupled with increasing industrialization of less developed nations and the justifiable expectations of their citizens, is placing enormous pressure on our environment through the production of vast quantities of solid, liquid and gaseous pollutants (which contribute to global warming).

Wastes pose a number of problems. They may contain hazardous elements and compounds, such as heavy metals, persistent organic pollutants such as dioxins and furans, pathogenic organisms or radionuclides. They may (like CO_2) simply be produced in such large volumes that the ecosystem can not correct the imbalance, or they may have size and shape which makes them difficult to capture, with implications for human health. Alternative applications and uses are needed for nonhazardous and inert wastes. If waste is hazardous and injurious to health, ways must be found to render it harmless or, as a last resort, immobilized in a wasteform suitable for long-term disposal.

Ceramics technology is contributing to the remediation and cleanup of pollution and has a key role in developing new reuse and recycling options for many wastes. The ceramics industry, when defined in the broadest possible terms, is one of the few industries processing high volumes of materials. Therefore, it has the capacity and potential to make a significant contribution to solving problems associated with wastes. Most inert wastes are oxides containing significant amounts of alumina, lime, magnesia, iron oxides and silicates and already find uses in high-volume applications in relatively low-technology materials

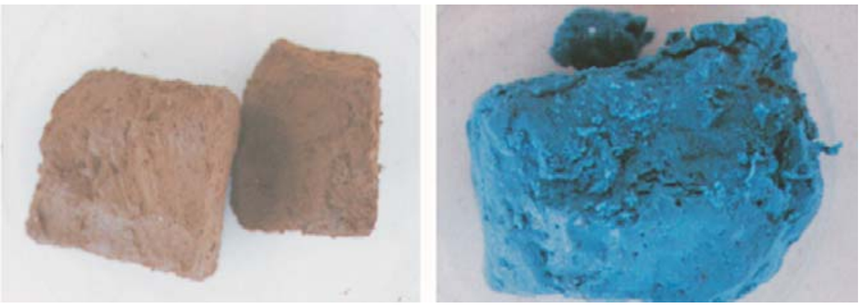

Figure 1. Fe-rich galvanizing sludge generated in the steel wiredraw production (left) and Cr/Ni-rich sludge generated from the Cr/Ni plating process (prepared in Aveiro).

João Labrincha is Associate Professor at the Department of Ceramics and Glass Engineering of the University of Aveiro and member of the CICECO research unit. Following his PhD he has implemented a research line in Wastes Recycling. Simultaneously he leaded the creation in the University of Aveiro of Pos-grad studies in that field. Other research interests include ceramic processing and optimisation (e.g. extrusion), new cement and mortar formulations. He published is a ca. 105 SCI papers and he is author or co-author of 17 patents applications.

used in road construction, roof tile, cements and concretes, and house brick applications in which they nonetheless can contribute significant savings in energy consumption, because they replace materials which otherwise need to be processed from the raw state. Others are being examined for uses in more advanced ceramics, including glass-ceramics, composites, magnetic ceramics, stoneware and porcelains, where they also can reduce use of natural mineral resources such as alkali fluxes.

In the future ceramics will increasingly play a key role in the achievement of sustainable development. Waste and recycled materials are being utilized extensively in high-volume ceramics such as glass, cements and many vitreous ceramics. Their use will be extended where economic or legislative drivers are present. There will be increasing use of wastes as aggregate in bound and unbound civil engineering applications. New ceramic products will arise and come to market manufactured from sinteredor melted wastes. Within a few years, we will see an emerging industry base (often small enterprises) that will take waste, sort and separate it and seek applications and potential markets. Because of the increasing cost of landfill, more waste incineration units are being built worldwide, and while there has been much research into applications for the ashes emanating from them a greater commercial take-up based on this research is needed.

Within the next five years, we expect to see development of cements that set by reaction with atmospheric CO_2: carbon negative cement systems. There will be increasing understanding of the potential of room-temperature glasses such as geopolymers and room-temperature ceramics such as phosphate cements. Cost-effective vitrification technologies will evolve for particularly problematic hazardous wastes, making them inert and beneficially reusable based on plasma or cold-crucible melting technologies. There is already a discernable shift in public opinion and marketing so that products made from secondary materials are seen as desirable, and this will continue. Major civil engineering projects in many countries will be assessed for their sustainability by the amount of secondary materials used in construction. In the 5–10 year time frame, we will see evidence of increasing globalization of research into, and implementation of, sustainable development. There will be growing realization of the importance of recycling and reuse of materials and immobilization of hazardous wastes. More international research programs in this area of the sort already in place in Europe will be initiated.

Figure 2. Examples of technical ceramics made from industrial wastes: glass-ceramics (left) and refractories based on Al-anodizing sludge (prepared in Aveiro).

Co-workers: Victor Ferreira, Ana Segadães, Manuel Ribeiro, Michele Dondi, Dachamir Hotza, Guillermo Monrós, Pedro Novaes Oliveira, Fabiano Raupp Pereira, Grácia Costa.

Figure 3. Examples of grey and black Co-free pigments fully based on industrial sludges (prepared in Aveiro).

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Microporous Transition-Metal Silicate Membranes

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The discovery of titanosilicates ETS-10 and ETS-4 prompted research into the synthesis of new families of zeolite-type materials with structures (usually) consisting of interconnected mixed polyhedra.[1] These materials possess novel structures presenting new possibilities for isomorphous framework substitution, while preserving their microporous structure and cation contents, thus allowing fine tuning the catalytic and adsorption properties of a given material. Many titanosilicates have strong basicity, in some way complementary to the acid properties of zeolites. The preparation of these materials in the form of membranes broadens the scope of potential applications. Their synthesis does not require organic molecule templates (in contrast with zeolites synthesis) and, thus, they are relatively unexpensive, environmentally friendly and membrane calcination treatments (which often lead to defects or loss of active surface groups) are not necessary. We have successfully prepared membranes of titanosilicates AM-2(umbite)[2,3] and ETS-10,[4,5] and vanadosilicate AM-6,[5] exhibiting a performance which affords them potential for real applications.

Titanosilicate AM-2 membranes for H_2 separation

Membranes of titanosilicate AM-2 with the umbite structure have been prepared (Fig. 1), ca. 5 μm thick layers, on porous α-alumina and TiO_2 tubular supports, by seeded hydrothermal synthesis. These membranes are able to separate H_2 from N_2, CO_2 and propane with good selectivity.[3] The selectivity for H_2/N_2 mixtures is as high as 48 (Fig. 2), even in the presence of water.[2] Such membrane may be of interest in the purification of H-containing streams and H_2 proton-exchange membrane fuel cells.

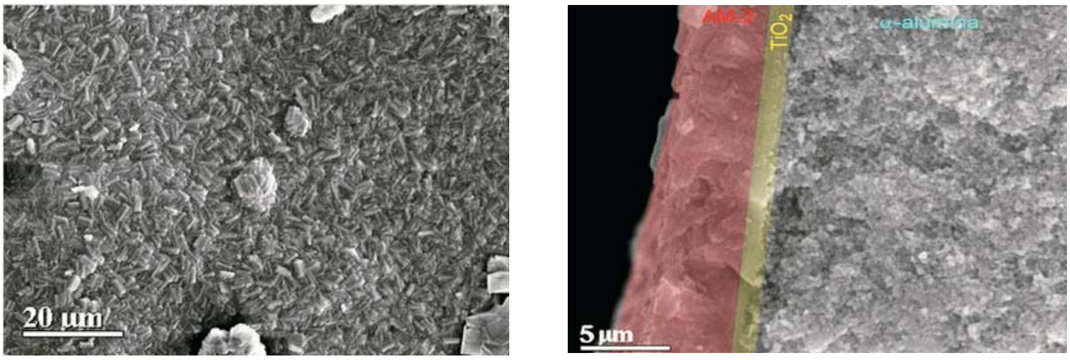

Figure 1. Cross section and top view of an AM-2 membrane.

Zhi Lin was born in 1960 in China. He is an Auxiliary Investigator of CICECO. He obtained his Ph.D. degree from the University of Aveiro in 1998, followed by a post-doc in the same place. Since 1994 he has been investigating new crystalline microporous materials. He was familiar with hydrothermal synthesis and characterization, especially by solid-state NMR and X-ray crystallography, of microporous silicates with stoichiometric amount of Ti, Zr, Sn and Hf. He published over 50 papers in this field. Recently he has been workeing on the applications of these new materials, particularly as membranes and ion exchangers and published 7 papers in this area.

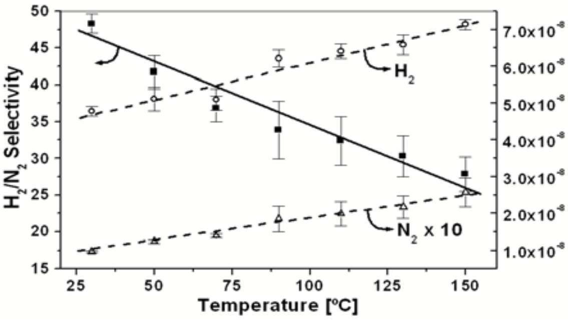

Figure 2. H_2/N_2 separation selectivity and H_2 and N_2 permeances through an AM-2 membrane as a function of temperature.

Titanosilicate ETS-10 membrane for the separation of water/organic mixtures

ETS-10 membranes have been prepared on porous **a**-alumina and stainless steel tubular supports. The c-in-plane preferentially orientated pure ETS-10 membranes (Fig. 3) ca. 5 **m**m thick were synthesized, exhibiting a good intergrowth of crystals (Fig. 4). Pervaporation experiments have been performed, yielding at 150 ºC a water/ethanol separation factor up to 12 and a water flux of 1.1 kg/(m^2·h). Due to the hydrophilic character of the solid, ETS-10 membranes may be used for the separation by pervaporation of water/organic mixtures.

Titanosilicate ETS-10 and vanadosilicate AM-6 membrane for propylene/propane separation

Defect-free and pure ETS-10 and AM-6 membranes, 4-7 m thick, with well intergrown crystals, were synthesized on porous **a**-alumina tubular supports. At room temperature, these membranes exhibit promising propylene/propane separation factors (3.8-6.5 for ETS-10 and ca. 2.3 for AM-6). Propylene is one of the most important raw materials in the petrochemical industry since it finds applications in the synthesis of products, such as polymers and propylene oxide. The main processes to obtain propylene yield a propylene/propane mixture. While distillation has been used to separate these products, it consumes much energy. Membrane separation is, in this context, an attractive alternative.

This research was carried out in collaboration with Prof. João Rocha (CICECO), Dr. J. Coronas and Prof. J. Santamaría (Zaragoza University, Spain).

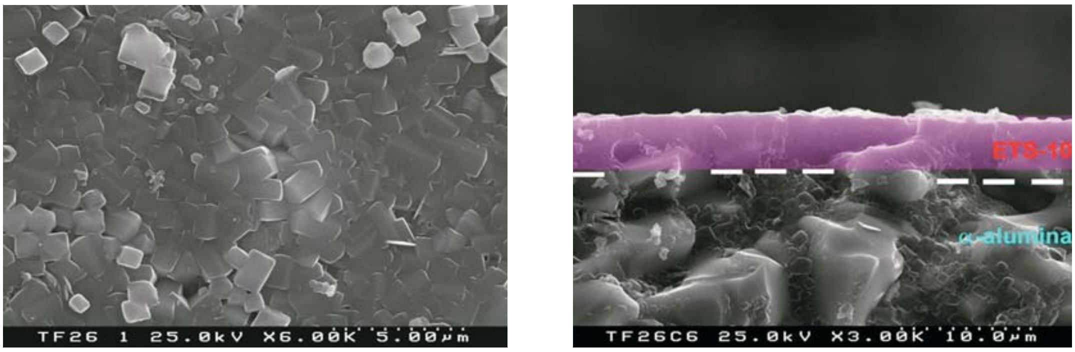

Figure 3. Cross section and top view of ETS-10 membrane.

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In Situ Diffraction Study of the Pressure-Temperature Phase Diagram of C_{60}

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The pressure-temperature phase diagram of C_{60} up to 8 giga-Pascal (GPa) and 800ºC, has been studied by in situ synchrotron diffraction methods. Under these pressure-temperature conditions, we have found the previously reported polymeric phases involving 2+2 cycloaddition intermolecular bonds. In addition, the use of 2D detector allowed to image the advance in the polymerisation process and revealed the fundamental role of the anisotropic applied stress in obtaining ordered polymeric structures.

C_{60} has a very rich pressure-temperature phase diagram: high-pressure phases consist of polymerised fullerene networks with a variety of structural architectures. High-pressure is thus a valuable method to create novel nanostructured carbon phases. Previously C_{60} high-pressure polymeric phases were identified and characterised in samples quenched down to ambient conditions. In this study we have probed directly their high-pressure stability and we have found the reason why the high-pressure polymers have an ordered nature, in contrast to the (disordered) photo-induced C_{60} polymers.

The present study was performed at the ID30 (now ID27) high-pressure beamline at the European Synchrotron Radiation Facility (E.S.R.F.) in Grenoble, France. The experimental set-up includes the Paris-Edinburgh large-volume pressure-cell and an image-plate detector. The use of synchrotron radiation is mandatory in this type of studies due to the small sample volume and the weak scattering power of carbon. Several polymeric C_{60} phases, 1D chains and 2D quadratic and triangular layers, were found below 8 GPa and at temperatures around 500-700ºC (Fig. 1). The observed pressure-temperature domain of each phase agrees with the previously proposed phase diagram, which was obtained with quenched samples. As expected, the most compressed phases are stable at higher pressures.

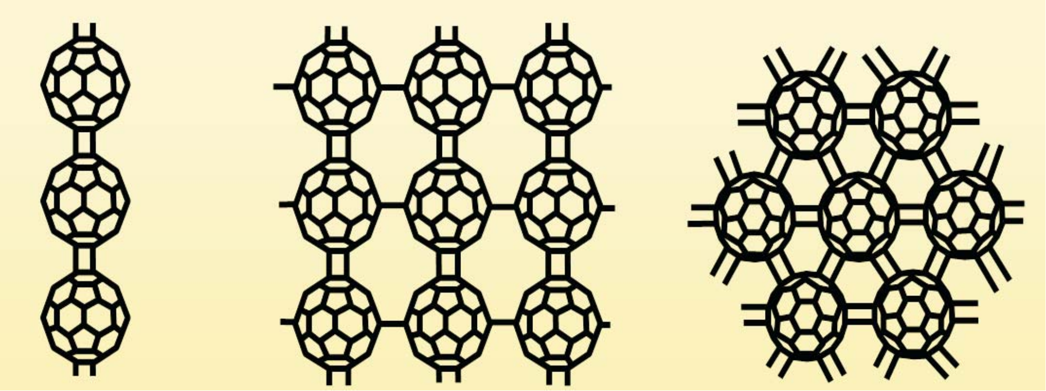

Figure 1. C_{60} polymeric high-pressure phases.

Leonel Marques got its PhD degree in Physics at the Joseph Fourier University, Grenoble, France. He is currently “Professor Auxiliar” of Physics at the University of Aveiro and Researcher at CICECO. He uses synchrotron radiation at the European Synchrotron Radiation Facility (E.S.R.F.) to study the pressure-temperature phase diagram of C_{60}, seeking new nanostructured carbon phases with interesting physical properties.

With this experimental technique we were able to follow the polymerisation process in detail. C60 polymerisation occurs as a homogeneous process where the growing polymer enters the monomer matrix statistically, without phase separation. The advance in the process is, therefore, reflected in the increase of lattice strain. In the early stages of the process 2D diffraction patterns become anisotropic. This distortion of the diffraction rings indicates that the polymerisation progresses at higher rates along the uniaxial component of stress, as schematically shown in Fig. 2 a. This trend is independent of grain orientation. The anisotropic bonding pattern within the partial-transformed sample is therefore a signature of the anisotropic stress applied to the sample during the process. On the other hand, full-transformed samples display transformation textures resulting exclusively from the polymerisation anisotropy (no grain rotation is observed). This indicates that further polymerisation progresses along the high-stressed directions until the formation of bonds is completed, while along the low-stressed directions the polymerisation stagnates (Fig. 2b). In summary, the anisotropy of the compression guides the polymerisation leading to the formation of ordered low-dimensional polymerised structures.

Above 8 GPa bonding schemes, other than then 2+2 cycloaddition, become active and 3D C_{60} polymers are formed. These structures are better viewed as carbon clathrates since these C_{60}-derived phases are no more molecular solids. These new nanostructured carbon phases are low-density low-compressibility materials and display metallic conduction. They are the subject of our current research.

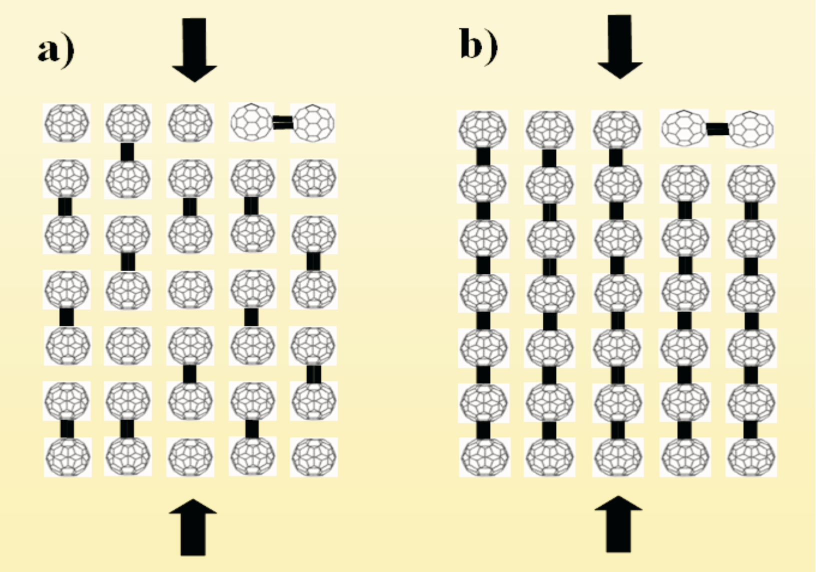

Figure 2. Polymeric-bonding pattern evolution during the polymerisation of a grain with the near-neighbour direction coincident with the uniaxial component of compression (indicated by arrows): a) at the initial dimerising stage, b) at the end of the polymerisation process.

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The High Industrial Pulping Performance of *Eucalyptus globulus* Wood is Due to Its Peculiar Chemical Structure

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Eucalyptus globulus wood is the main raw material of the Portuguese pulp-and-paper industry. In the last few years, the using of this hardwood is increasing enormously worldwide because of its remarkable properties. In the industrial pulping process, fibres are isolated by degradation and dissolution of most of wood lignin, followed by the removal of residual chromophores (bleaching), preserving as much as possible polysaccharides (cellulose and hemicelluloses). Among the different industrial hardwoods, *E. globulus* is known to afford high pulping yields and requiring low reagent charges in the pulping and bleaching processes, thus reducing production costs and environmental impact of the pulp mill.

Such behaviour was poorly understood, mainly because of the lack of knowledge on the chemical composition and structure of wood components. Research initiated at the University of Aveiro inthe mid nineties and strongly consolidated in the last 5 years, within the scope of CICECO, allowed a deep understating, at the molecular level, of the peculiar structural features of *E. globulus* wood components.

Lignin, polysaccharides and low molecular weight (extractible) compounds were submitted to structural studies, calling upon the most state-of-art techniques, some of them (ca. ESI-MS), used for the first time in structural studies of complex biopolymers such as lignin. The detailed structure of lignin was elucidated, showing a macromolecular structure extremely rich in syryngylpropane derived moieties, low degree of crosslinking and high content of arylglycerol eter linkages (Figure 1). The *E. globulus* 4-*O*-methylglucuronoxylan (most abundant hemicellulose), showed a peculiar structure, reported by our group for the first time, quite different from other hardwoods xylans, bearing *O*-2 substituted 4-*O*-methylglucuronic moieties.

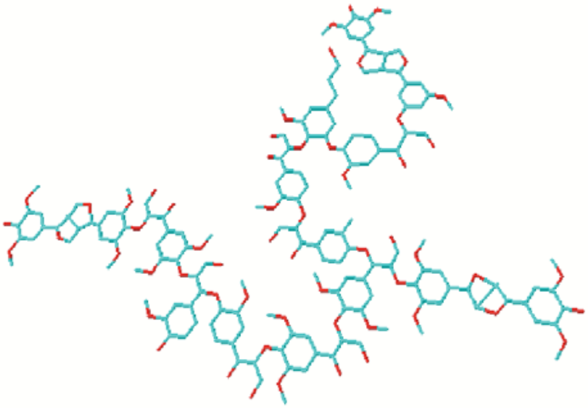

Figure 1. Structure of a fragment of Eucalyptus globulus lignin macromolecule.

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Dmitry V. Evtuguin is Associate Professor at the Department of Chemistry of the University of Aveiro since 2001. Graduated in Engineering and Chemical Technology, specialty Chemical Processing of Wood, by the Leningrad Forest Technical Academy (LFTA), USSR (1985). Candidate of Chemical Science (PhD) in Chemistry (Wood Chemistry) by LFTA, USSR (1988). Author/ co-author of 95 articles and book chapters, 145 conference communications and 4 patents.

Latter, in cooperation with the industrial sector, similar studies were carried out for other industrial hardwoods as well as for laboratory and industrial pulps collected at different stages of the pulping and bleaching processes.

Results obtained allowed to correlate the industrial pulping and bleaching performance with the chemical features of wood and pulps. The low chemical charges required in pulping and bleaching and processes are assigned to the extremely reactive lignin structure (see, as an example, Figure 2 for the correlation between the proportion of syringylpropane/guaiacylpropane units in unbleached pulp lignin and the amount of ClO_2 required to bleach the pulp). The peculiar xylan structure, involving linkages to other cell wall polysaccharides, was shown to contribute to the high retention of this polysaccharide during the pulping, thus improving the pulp yield.

The information gathered along the last decade on E. globulus chemistry allowed a rational understanding of the processes associated to the transformation of wood into pulp and is now contributing to improve established industrial processes as well as to the development of new efficient delignification systems, using this wood as a raw material.

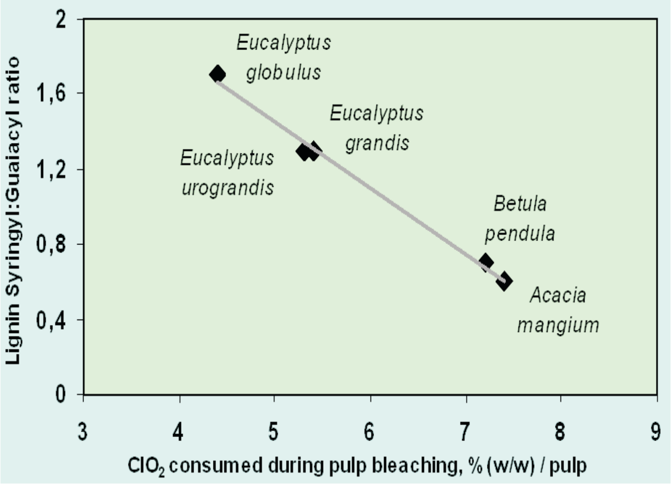

Figure 2. Relationship between the proportion of syringyl/guaiacyl units in Eucalyptus globulus kraft pulps lignin and the bleaching ability.

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New Structural Motives in Polyoxometalate Chemistry

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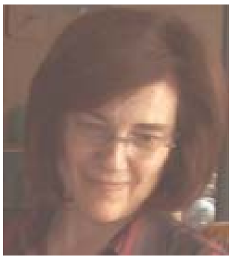

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Polyoxometalates are metal-oxoclusters built up from basic octahedral MO_6 units (M = Mo, W, V) that may also assemble by bonding to other chemical elements. The chemical variety and richness of properties found for this type of compounds are an outcome of the numerous structural possibilities. A very important structural set, found in a large range of compounds, is that of the Keggin-anions $[XM_{12}O_{40}]^{n-}$ (X = B, Si, P; M = Mo, W) and its lacunary forms. A new form of a lacunary Keggin-anion, the 1,4-bilacunary $[PW10O38]^{11-}$, was first reported by us in the compound $H_7K_{10}Ce_2(PW_{10}O_{38})(PW_{11}O_{39})$×$28H_2O$.[1] This structural motif presents new bonding possibilities, namely in the coordination to lanthanides, as shown in the crystal structure reported (Fig. 1). The structural assembly is closely related to properties such as photoluminescence and catalytic behaviour that we have been studing.

Following our interest in the synthesis and structural characterisation of new lanthanide complexes of polyoxometalates as well as in their applications in photoluminescent materials or as catalysts for oxidation reactions, we investigated the less studied polyoxotungstoborates (when compared to the respective phosphates or silicates). A novel one-dimensional zigzag lanthanopolyoxotungstoborate was synthesised, $H_2(NH_4)_{10}[Ce_2(BW_{11}O_{39})_2(H_2O)_6]$×$21H_2O$,[2] being the first example of a coordination polymer where monolacunary Keggin-anions containing a central boron atom are bridged by Ce^{3+} cations. The related Eu^{3+} compound was used in the assembly of a photoluminescent nanostructured film.[3]

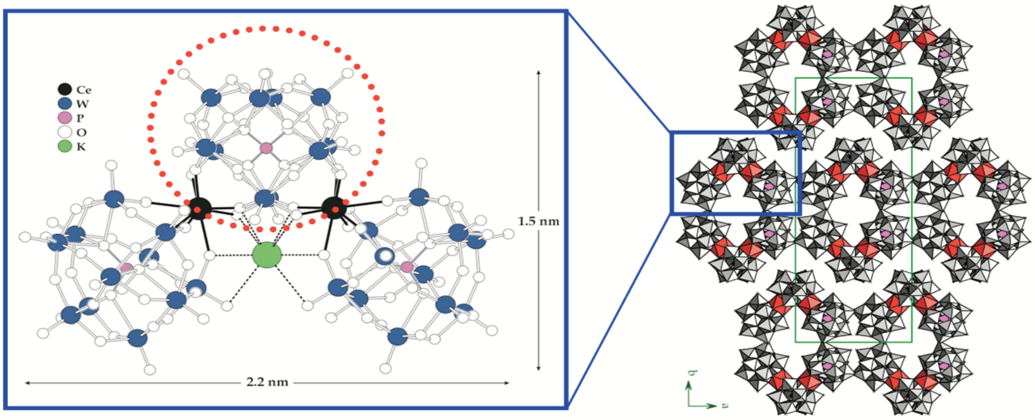

Figure 1. Crystal structure of $H_7K_{10}[Ce_2(PW_{10}O_{38})(PW_{11}O_{39})_2]$×$28H_2O$.

Helena I. S. Nogueira is Auxiliary Professor at the Department of Chemistry of the University of Aveiro since 1997, being a member of the Department staff from 1990. After a Ph.D. at the Imperial College of Science Technology and Medicine, University of London, UK (1996), she has been developing research on the coordination chemistry of second and third row transition metals and the lanthanides with a particular interest on the synthesis of lanthanopolyoxometalates for the preparation of new nanostructured luminescent materials and hybrid organic-inorganic functional materials. Other research areas include Raman spectroscopy, in particular SERS, and heterogeneous catalysis.

Ana Cavaleiro has a degree in Chemical Engineering from the University of Lisbon (IST), a M.Sc. in Chemistry from the University of Liverpool and a Ph.D. in Inorganic Chemistry from the University of Aveiro. She started her professional career in 1968 at the University of Lourenço Marques, Moçambique and joined the University of Aveiro in 1975. In 1999 she obtained her “Agregação” at the University of Aveiro. Since 2003 she has been full Professor in the area of Inorganic Chemistry. Her current research interests focus on the chemistry of polyoxometalates, especially on the development of new materials with polyoxometalates and the preparation and study of polyoxometalate compounds with organic entities with potential applications in catalysis, electrochemistry, non-linear optics and others.

A new structural family of monolacunary Keggin-type polyoxotungstates containing Ag^{I} metallic centres was found with the compound $H_2Ag_{0.33}K_{3.67}[AgPW_{11}O_{39}]×8.25H_2O×CH_3OH$.[4] A chain-like silver polyoxotungstophosphate was formed when Ag^{I} centres, exhibiting an unusual eight-coordination, bridge a monolacunary [PW11O39]$^{7-}$ anion, through the lacuna, to a neighbouring lacunary **a**-Keggin anion by a less common bonding to four **m**$_2$-oxygen atoms (Fig. 2).

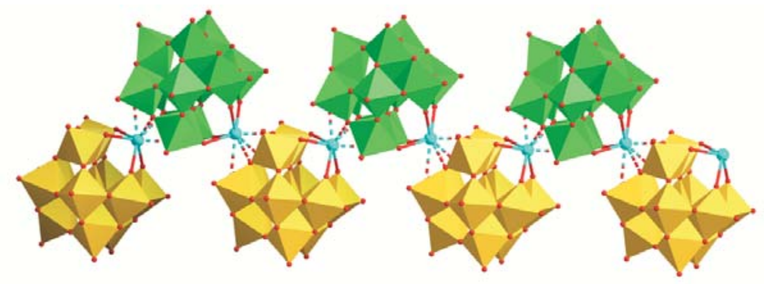

Figure 2. One-dimensional anionic $[AgPW_{11}O_{39}]_n^{6n-}$ chain.

The polyoxometalates presented above have been used as functional units in the preparation of new materials such as nanostructured thin films [3] or luminescent clays. A new project is underway concerning the preparation of polyoxometalate based organic-inorganic hybrid materials (POCI/QUI/58887/2004 financed by FCT).

New motives and structural patterns may result from the association of polyoxometalates with organic molecules. Fig. 3 represents the structure of $(2A5NP)_4H_3[PMo_{12}O_{40}]•2.5H_2O•0.5C_2H_5OH$ (2A5NP = 2-amino-5-nitropyridine). This compounds has an unusual structure that may be described as a supramolecular aggregate composed of ordered Keggin anions surrounded by one-dimensional ribbon-like chains of 2A5NP and water molecules, held by intermolecular hydrogen bonds.[5] The study of this and related compounds is being pursued in the search of materials with interesting charge-transfer or non-linear optical properties.

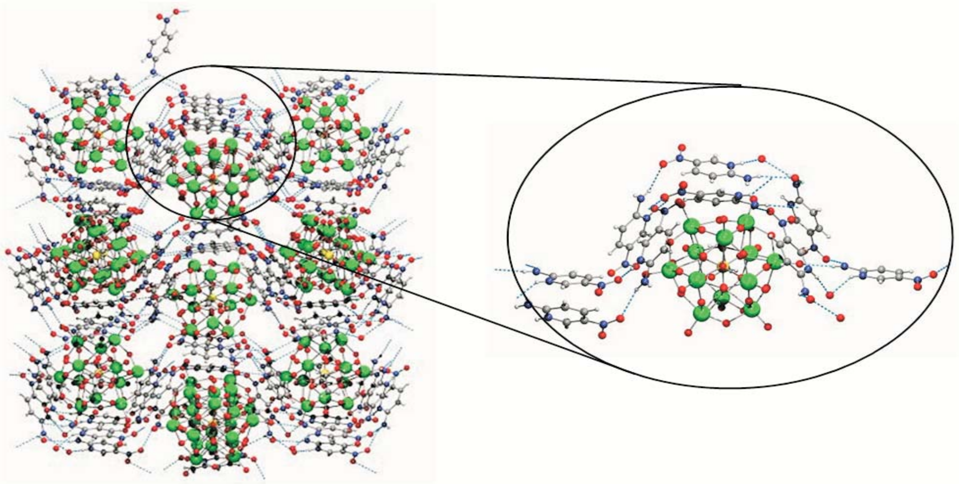

Figure 3. Crystal structure of $(2A5NP)_4H_3[PMo_{12}O_{40}]•2.5H_2O•0.5C_2H_5OH$.

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Functional Crystalline Lanthanide-Organic Frameworks

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The molecular design of novel coordination-based functional multi-dimensional (i.e., 1D, 2D and 3D) materials has seen an enormous surge of research interest in the last two decades. The initial promise of a completely new approach to the isolation of scaffolding-type compounds, in which organic and inorganic components could co-exist in one functional material, attracted scientists from many different areas. However, chemical crystallographers had a key role in the development of such research area since the intriguing structural architectures could only be unequivocally described by single-crystal diffraction methods, in particular that of X-rays. More recently, a handful of laboratories around the world started to devote their attention to the materials which are usually isolated as microcrystalline powders. Indeed, many of these materials were revealed to be highly interesting, sharing striking similarities from the functional point of view with, for example, zeolites and mesoporous phases.

At CICECO, we have been particularly interested in the combined use of (poly)phosphonic acid ligands (sometimes along with carboxylic acid groups) with lanthanides to produce novel two- and three-dimensional networks. While the use of lanthanides (such as Eu^{3+}, Sm^{3+} and Tb^{3+}) is of great interest because it allows the immediate engineering of photoluminescent materials, (poly)phosphonic acid ligands provide on the other hand great connectivity between metallic centres. Indeed, far more than carboxylic acid groups (commonly using in the synthesis of this type of compounds), the presence of tetrahedral-distributed oxygen atoms increases the number of possible coordination fashions.

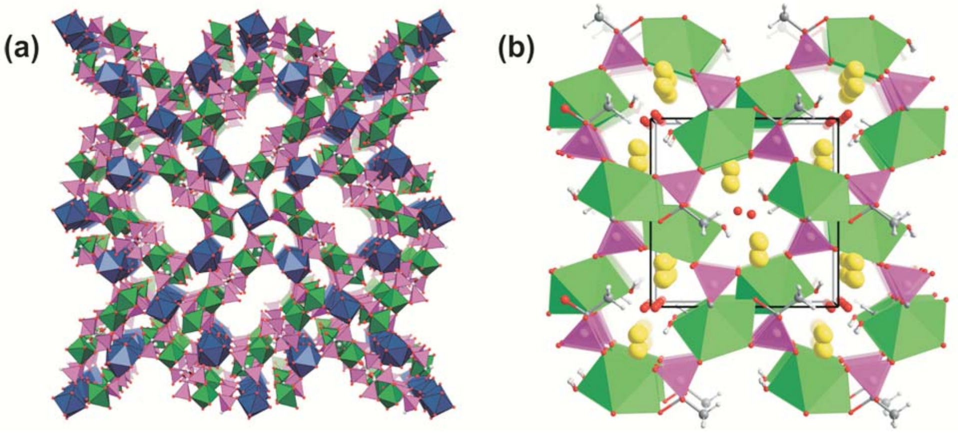

Figure 1. Crystal packing of
(a) $Ln_{1.5}[\{VO(\mu_2\text{-}H_{0.75}L)\}_3(\mu_3\text{-}O)]_{2/3}[\{V(OH)(\mu_2\text{-}HL)\}_3(\mu_3\text{-}O)]_{1/3}(H_2O)_9\cdot n(H_2O)$ *and*
(b) $Na_2[LnL(H_2O)]\cdot \frac{1}{2}H_2O$

Filipe A. Almeida Paz has a Ph.D. from the University of Cambridge (U.K.), where he studied under the orientation of Professor Klinowski working on the hydrothermal synthesis and structural characterisation of novel metal-organic frameworks, along with the chemical evaluation of hypothetical zeolitic-type frameworks enumerated systematically using tiling theory. His first degree is in Analytical Chemistry from the University of Aveiro (Portugal) where he is now a full-time Researcher in CICECO working mainly in X-ray chemical crystallography (both single-crystal and powder) and in the hydrothermal synthesis of novel hybrid materials. He is a regular referee for a number of international journals (which include Angewandte Chemie, Journal of the American Chemical Society and European Journal of Inorganic Chemistry) and the author (or co-author) of more than 90 publications.

Etidronic acid (hereafter designated as H_5L) is a diphosphonic acid ligand, and was found to form with V^{4+} a highly disordered cyclic trinuclear complex formulated as $[\{VO(\mu_2\text{-}H_{0.75}L)\}_3(\mu_3\text{-}O)]_{2/3}[\{V(OH)(\mu_2\text{-}HL)\}_3(\mu_3\text{-}O)]_{1/3}^{-4.5}$. We have used this anionic complex as a secondary building unit, self-assembling it in aqueous media and at ambient temperature (typical one-pot synthesis approach) with lanthanide centres to form impressive three-dimensional and highly porous open frameworks (Figure 1a): $Ln_{1.5}[\{VO(\mu_2\text{-}H_{0.75}L)\}_3(\mu_3\text{-}O)]_{2/3}[\{V(OH)(\mu_2\text{-}HL)\}_3(\mu_3\text{-}O)]_{1/3}(H_2O)_9 \cdot n(H_2O)$. The structurecontains one-dimensional channels which house a significant number of water molecules. In the absence of V^{4+}, we discovered that the same organic molecule self-assembles directly with the lanthanide centres, forming a rather distinct three-dimensional framework, $Na_2[LnL(H_2O)] \cdot ½H_2O$ (Figure 1b), which is prone to the reversible removal of the water molecules directly coordinated to the metallic centres. Indeed, such process could be directly followed by photoluminescent studies, thus rendering this material as a water sensor. Moreover, this material has a remarkable structural stability, with the dehydrated phase being stable almost up to 500ºC, always with the structural possibility to revert to the original phase by simply leaving the compound under a humid atmosphere. Another remarkable structural feature of this material is the presence of sodium lying inside the channels. This feature is typical of zeolites, and it is not unfeasible to assume that the remarkable structural flexibility observed for these materials is indeed partially due to the robustness achieved by the presence of these chemical species. Structures belonging to these two families of three-dimensional hybrid frameworks could only be elucidated by using single-crystal X-ray diffraction and by applying sophisticated refinement strategies, usually only employed for macromolecular structures, i.e., proteins. This was particularly important for the former framework due to the highly disordered nature of the water molecules inside the channels.

When larger organic molecules containing two or three distinct phosphonic acid groups were self-assembled with lanthanides no single-crystals could be isolated. Instead, microcrystalline powders were systematically obtained. Nevertheless, in the case of nitrilotri(methylphosphonic acid) (H_6NMP), compounds showed reversible water removal with negligible changes in the photo-luminescence spectra, thus rendering the materials immune to the hydration level. The structure, ultimately formulated as $[Ln(H_3NMP)] \cdot 1.5(H_2O)$ (Figure 2), could only be unveiled by applying sophisticated *ab initio* strategies based on high-resolution powder X-ray diffraction data (collected at a synchrotron source) in conjunction with structural information derived from solid-state NMR studies. Future by research involving these systems contemplates the fine tune of the photoluminescent properties by including in the interlayer space organic molecules which could sensitize the lanthanide centres. Moreover, the close spatial proximity between lanthanide centres imposed by the phosphonic acid groups opens the possibility to engineer materials which could simultaneously exhibit photoluminescent and magnetic properties.

Some of the work described above was performed in collaboration with Professor J. Rocha and his research group.

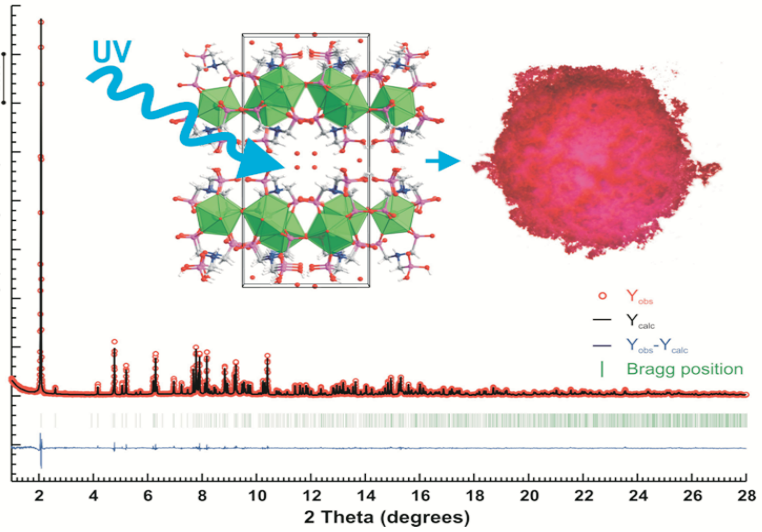

Figure 2. Rietveld plot (synchrotron data – BM01b beam line - ESRF) and crystal packing of $[Pr(H_3NMP)] \cdot 1.5(H_2O)$. Photoluminescence (in the visible region) of the isostructural material

Nanoscale Control and Investigation of Individual Nanoparticles on OpticallyActive Group III-N Low Dimensional Structures

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We have been researching new routes to the unification of the two main strategies to produce ensembles of well-defined inorganic nanocrystals, which promise enormous potential for future optoelectronic and spintronic devices. With a dual approach combining flexible wet chemistry with traditional semiconductor processing, this study aims to develop the knowledge to pursue alternative ways to create new heterostructures incorporating colloidal nanocrystals. Specifically, we are combining multiple-quantum wells (MQWs) and colloidal nanoparticles and quantum dots (QDs), in such a way that the best properties of each system may be exploited. In this way, we intend to introduce disruptive innovation in the field and open the door to the integration of several different functions in one device.

The different methods used to fabricate quantum nanostructures usually emerge from distinct scientific backgrounds; physicists mainly favour “top down” approaches while chemists prefer “bottom up” methods. This dichotomy of approaches results in a technology gap between the two strategies used to produce nanoparticles, namely physical deposition, such as molecular beam epitaxy (MBE), and wet chemical synthesis. However combinations of such approaches, as complementary realms of activity, offer the possibility to achieve novel functional nanomaterials and also give new scientific insights of a more fundamental kind; bridging the technology gap will open the way to the engineering of material systems that can offer radically new properties in particular through the exploitation of cross-coupling effects, with an unrivalled flexibility.

By combining facilities and taking advantage of the complementary expertise available in the research groups based in CICECO, the present work aims to bring together and study interactions between QDs produced by lyothermal routes and nitride-based MQWs, grown epitaxially on sapphire substrates. Within this research program we are also developing innovative methods to enable the positioning of clusters of a few nanoparticles, down to individual nanoparticles on the surface of epitaxial heterostructures. The laboratory and stage for our approach is provided by the spontaneous formation of intrinsic nanoscale defects (Inverted Hexagonal Pits) in indium-containing III-nitride heterostructures.

Group-III nitrides are typically grown for commercial applications on lattice-mismatched sapphire by means of MOVPE. However, when In is to be incorporated into such layers, the volatility of InN and the large vapor pressure of N requires the use of temperatures, much lower than are used for growing GaN. At such low temperatures, even small perturbations of the surface tend to produce (inclined) facets with the lowest growth rate, i.e., (1-101) facets. This occurs preferentially at the apex of threading dislocations, where V-shaped hexagonal pits with (1-101) sidewalls form.[1-5] Experimental analysis of the film surface using atomic force microscopy (AFM) reveals the morphology of these remarkable hexagonal pits (Fig. 1).

The pit depth (which is related to the lateral size through the geometry of the wurtzite structure) may be tuned by adjusting the layer thickness above the critical layer thickness for pit formation. The pit formation for this particular InGaN/GaN MQW occurs only after growth of the 9th well (Fig. 2).

Sérgio Pereira, age 30, has a PhD in Physics and has joined the CICECO research team in early 2006. His research interests span the whole range of applied solid state Physics; however most active areas under investigation in the last years have been focused on the development of nanostructured materials for optoelectronic applications. He has been actively involved in the development and application of nanoscale characterization techniques for strain and composition analysis of thin films of advanced materials including; X-ray diffraction, Rutherford backscattering and optical spectroscopy.

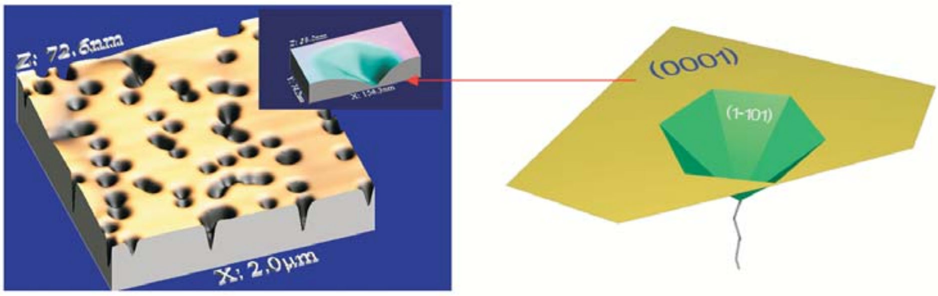

Figure 1. Atomic force microscopy micrograph showing a large density (~1x10^8/cm^2) of pits at the surface of an InGaN/GaN multiple quantum well (MQW) structure. The inset shows the profile of one of the nano-pits in detail. The right panel shows a schematic view of a hexagonal V-shaped pit emerging at the apex of a threading dislocation in an InGaN-based heterostructure.

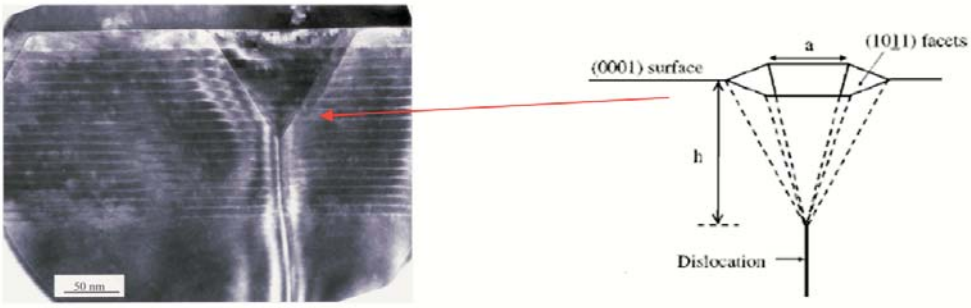

Figure 2. Cross-sectional Transmission Electron Microscopy (TEM) of an InGaN/GaN MQW evidences the periodic 18-well structure and shows clearly a threading dislocation that starts near the 9th well to form an IHP which is observed at the surface.

The possibility to control the depth of IHPs allows the number of nano-scale objects “trapped” at each pit to be adjusted. The density of these IHPs, which is intimately connected to the threading dislocation density, may also be controlled. Our method integrates colloidal nanoparticles into epitaxial heterostructures and has been successfully applied to isolated gold nanocrystals (Fig. 3).

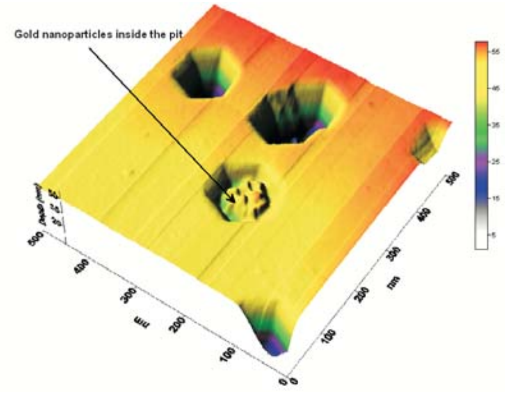

Figure 3. AFM image of a nanoscale pit filled with several gold nanoparticles.

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Layered Double Hydroxides as Hosts for Metallo-Organic Complexes

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Layered double hydroxides (LDHs) are unusual layered host materials. In contrast to clay minerals with negatively charged layers, such as 2:1 phyllosilicates, the layered structure of an LDH is built by the periodical stacking of positively charged metal hydroxide layers, typically containing M^{2+} and M^{3+} cations, and negatively charged interlayers consisting of anions and water molecules. The anions can be replaced by other species through an ion exchange process. We have been studying LDHs as hosts for catalytically active or photofunctional metal complexes of chelating ligands,[1] with the aim of preparing multifunctional inorganic-organic nanocomposites where the properties and even the structures of the guest species may be uniquely controlled by the host-guest interaction and the precisely defined environment of the interlayer. A largely unexplored method for the synthesis of LDHs intercalated with metal complexes involves the formation of the complex between the host layers following intercalation of a ligand. We studied the anion 2,2'-bipyridine-5,5'-dicarboxylate (bpydc) for this approach, since bipyridine is an effective chelate ligand for a broad variety of metal ions. A Zn-Al LDH was intercalated by bpydc anions by ion-exchange of a precursor material in nitrate form.[2] The basal spacing of the layered host increased from 9 to 18 Å and this suggested that the organic anions were arranged with their longest dimension nearly perpendicular to the host layers (Fig. 1).

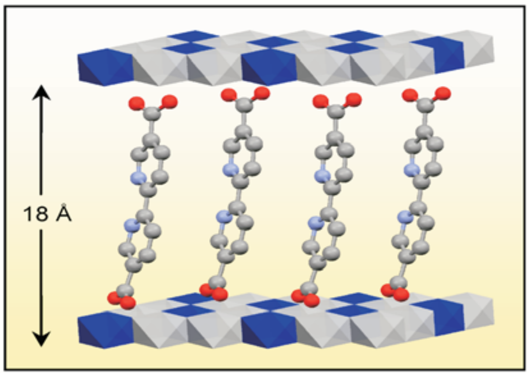

Figure 1. The likely arrangement of 2,2'-bipyridine-5,5'-dicarboxylate anions in the interlayer region of the Zn-Al LDH intercalate (H-atoms for the guest have been omitted for clarity).

Zn-Al-bpydc was used as a nanoporous matrix to take up $LnCl_3$ (Ln = Eu, Gd) from solution.[2] In order to characterise the average local coordination environment of europium centres in the material Zn-Al-bpydc/Eu, EXAFS studies were carried out at the European Synchrotron Radiation Facility. Analysis of the Eu L_3-edge EXAFS data revealed one shell of 7 ± 1 oxygen/nitrogen atoms at 2.41 Å and no evidence for a Eu–Cl bond (Fig. 2).

Photoluminescence studies provided further information about the nature of the Eu^{3+} first coordination sphere. The emission spectra displayed the typical Eu^{3+} red emission and showed the existence of only one type of Eu^{3+} binding site. The quantum efficiency of the first excited state ($^5D_0$) was estimated to be low (7.7%), due to a relatively high non-radiative transition probability caused by the presence of water molecules in the first coordination shell. The number of water molecules was calculated as 3.6 ± 0.1. We were therefore able to deduce that the incorporated europium ions were 6- or 7-coordinate with 4-5 oxygen atoms from water molecules and two nitrogen atoms from a bidentate bipyridyl ligand (inset in Fig. 2).

Martyn Pillinger received his degree in chemistry from the University of Southampton in 1990 and completed his Ph.D. at the same University in 1994 under the supervision of Prof. J. Evans, working on EXAFS studies of pillared clays. This was followed by post-doctoral work with Prof. C. C. Romão at the Instituto de Tecnologia Química e Biológica (1994-1995), Prof. A. Dyer at the University of Salford (1996-1999) and Prof. João Rocha at the University of Aveiro (1999-2002). In 2002 he was appointed as an investigator at CICECO. His research interests centre on the host-guest chemistry of porous and layered materials with emphasis on the synthesis and characterisation of novel hybrid assemblies.

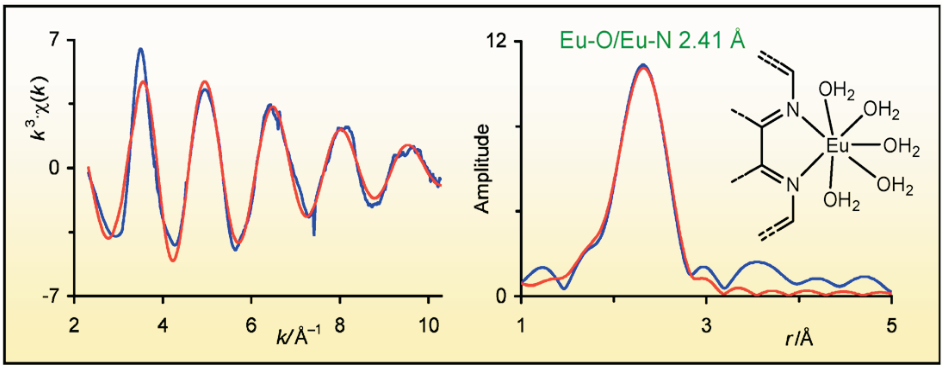

Figure 2. Eu L_3-edge EXAFS and Fourier transform of Zn-Al-bpydc/Eu (––– experimental, ––– theory). The inset represents the proposed Eu^{3+} average local coordination environment.

The potential of the pillared LDH Zn-Al-bpydc to act as a solid state complexation material led us to study its interaction with the complex $[MoO_2Cl_2(THF)_2]$.[3] The latter is known to undergo easy replacement of the tetrahydrofuran ligands by other organic donor ligands, giving complexes which are catalysts for the epoxidation of olefins. The immobilisation of these complexes on a suitable support is highly desirable in order to facilitate catalyst separation and recycling. Treatment of Zn-Al-bpydc with a solution of $[MoO_2Cl_2(THF)_2]$ gave a material with a high molybdenum loading of 11.2 wt.%. However, molybdenum K-edge EXAFS analysis could not substantiate the formation of a supported complex of the type $[MoO_2Cl_2(bpy)]$ and instead indicated the formation of oxygen-bridged dimeric species of dioxomolybdenum(vi) containing the $[O_2Mo\text{-}O\text{-}MoO_2]$ core, with a metal-metal separation of 3.29 Å. The material was found to be a selective and recyclable heterogeneous catalyst for the liquid-phase epoxidation of olefins.

The above results demonstrate that, although the material Zn-Al-bpydc has a high encapsulating ability for metal ions and complexes, the prediction of the final guest structures is nontrivial. A more controlled approach may involve direct intercalation of an anionic metal complex. To this end, we synthesised oxomolybdenum(VI) and oxotungsten(VI) complexes of 3,4-dihydroxybenzoic acid (3,4-dhb) with the general formula $[MO_2(3,4\text{-dhb})_2]^{2-}$. The complex anions were incorporated into Mg-Al and Zn-Al LDHs by ion-exchange reactions with precursor materials in nitrate form.[4] Elemental analysis and vibrational spectroscopy supported the successful intercalation of structurally intact complexes (Fig. 3). Possible applications for these hybrid materials lie in the field of heterogeneous oxygen atom transfer reactions.

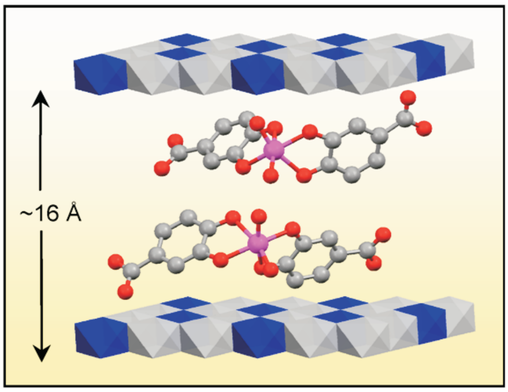

Figure 3. The likely arrangement of $[MoO2(3,4\text{-dhb})2]^{n-}$ anions in the interlayer region of Mg-Al and Zn-Al LDH intercalates.

Ongoing work is focussed on the preparation of new families of catalytically active oxomolybdenum and oxotungsten complexes that may be suitable as guests for LDHs. These will include species bearing chiral organic ligands for possible applications in asymmetric olefin epoxidation. We are also continuing our efforts to prepare luminescent materials through the immobilisation of lanthanide complexes in LDHs.

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1) This work would not have been possible without the invaluable contributions made by several students and colleagues at CICECO (their names appear in the following references).

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Rare Earth-Based Lamellar hybrid Nanoparticles

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The present requirements for phosphors demands for high emission efficiency and for lower energy excitation compared to standard materials used in luminescent lamps, flat screens, television and biological labeling. However, in order to comply with such requirements new materials are needed. In fact, standard phosphors are based on the absorption due to a charge transfer mechanism related to the excitation of an electron from the oxygen 2*p* orbital to the 4*f* orbitals of a lanthanide (Ln^{3+}) ion which generally takes place at around 250 nm (i.e. 5 eV).[1]

In order to decrease the required excitation energy materials based on different absorption physical processes are needed. A good approach is to use the larger absorption cross sections and low energetic absorptions of organic molecules to absorb the incident radiation which will be further transferred to the emitting lanthanide ions. However, lanthanide complexes are known to be unstable under a UV excitation.

In the last few years it was shown that non-aqueous sol-gel reactions of benzyl alcohol with different metal oxides precursors (alkoxides, chlorides, acetylacetonates,...) allow the controlled and straightforward synthesis of various crystalline metal oxide nanoparticles.[2]

At CICECO a new general non-aqueous sol-gel route has been applied for the preparation of rare earth (RE) ordered nanocrystalline hybrid structures. In a simple one-pot reaction process, RE(III) isopropoxides (RE= Y, Er, Gd, Sm, Nd) were dissolved in different alcohols and reacted in an autoclave between 250 and 300 ºC.[3-6] This approach leads to very thin (~0.6 nm) crystalline lanthanide oxide layers regularly separated from each other by organic layers of intercalated organic carboxylate molecules derived from the oxidation of the alcohol used as solvent (the thickness of the organic part is typically between 1.2 – 2.0 nm).

Fig. 1 shows transmission electron microscopy (TEM) images of yttria and gadolinia nanohybrid materials based on benzoate and biphenolate organic moieties. It is surprisingly that for each rare earth element and alcohol used a very similar behaviour is found. In the images the typical fringes produced by alternate contrast characteristic of the lamellar phase are well pronounced and the ordered structure extent over several lamellae.

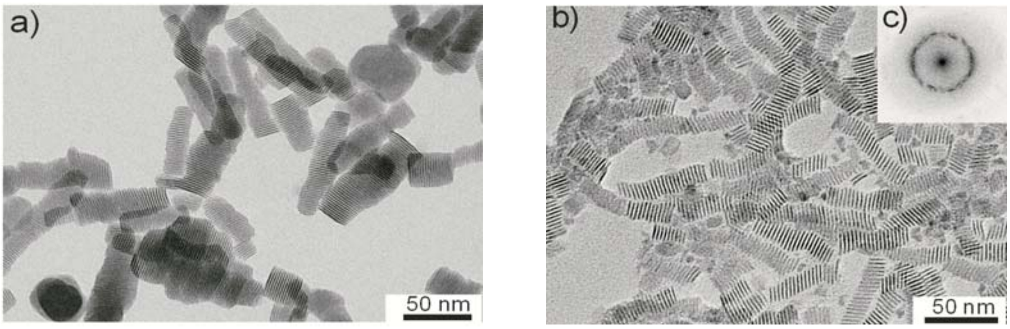

Figure 1. TEM images of the yttria-based benzoate (a) and of the gadolinia-based biphenolate b) nanohybrid materials. The Fourier transform of (b) shows the characteristic spots due to the lamellar order (c).

Nicola Pinna, chemist, senior researcher, received his degree in physical chemistry in 1998 and his PhD in 2001 from the University Pierre et Marie Curie (Paris, France). In 2002, he went to the Fritz Haber Institute of the Max Planck Society (Berlin, Germany). In 2003, he joined the Max Planck Institute of Colloids and Interfaces (Potsdam, Germany). In 2005, he joined the Martin Luther University, Halle-Wittenberg (Halle, Germany), as an associate professor of inorganic chemistry. Since 2006 he is senior researcher at CICECO. His research activity is focused on the synthesis of nanomaterials by non-aqueous sol-gel routes, their characterization and the study of their physical properties.

The oxidic part (i.e. the one who scatters strongly the incident electrons) is seen as dark layers. At opposite the organic material stays practically invisible between those layers. The as synthesized nanohybrid materials show good thermal stability for temperature up to 450 °C.

The optical properties of such nanohybrid materials doped with various lanthanides emitting ions were evaluated.[3-5,7] It was found that an efficient charge transfer from the organic moieties (benzoates and biphenolates) to the Ln^{3+} emitting ion takes place. By following such an excitation path the energy required in order to sensitize the luminescent ions is significantly lower that the one needed by similar pure inorganic compounds. Such a behavior is clearly seen in the excitation spectra of the different materials (Fig. 2) where the excitation peaks become broader and shift toward the large wavelength for the nanohybrids compared to the standard phosphors. Furthermore, because the absorption cross section of the intercalated organic molecules is much larger than the one of the charge transfer mechanism related to the excitation of an electron from the oxygen 2p orbital to the 4f orbitals of a Ln^{3+} ion the radiance (i.e. the emission brightness) observed is larger (up to 50%) than the one observed in standard phosphors used in luminescent lamps, screens, etc. Finally due to the presence of organic molecules which naturally emit in the blue and green region of the visible spectrum the emission chromaticity (i.e. the color) can be tuned by the excitation energy without losing the high radiance values.

In conclusion, we synthesize new luminescent nanohybrid materials that, from an emission efficiency and chromaticity point of view, exceed commercial phosphors.

This is a collaborative work with student M. Karmaoui, Dr. R. A. S. Ferreira and Prof. L. D. Carlos.

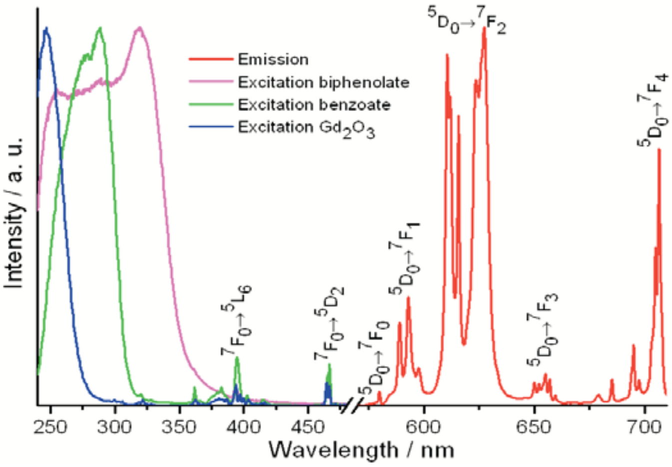

Figure 2. Emission spectrum of the gadolinia-based biphenolate nanohybrid materials (red) excited at 320 nm, its excitation spectra monitored at 612 nm (magenta), the one of the gadolinia-based benzoate nanohybrid (green) and pure Gd_2O_3 phosphor (blue).

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Cooperativity and Its Time-Scale, Temperature and Excitation Dependences: Describing and Predicting How Materials Behave

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The following has been achieved:

(1) Prediction of individual process and average frequencies within materials' structure - Fig.1;

(2) Prediction of their relative weight (materials frequency, or characteristic time, spectrum), including a quantitative measure of the changes in effective cooperativity (as measured by the sizes, n, of active clusters of structural elements) with temperature - Fig. 2 - and the time scale of the experiment/observation;

(3) Prediction of time-, temperature- and excitation-dependent responses in e.g. mechanical creep, that naturally turn out consistent with KWW dynamics and accurate time-temperature superposition at not too low temperatures –VTF, or WLF, at low to moderate temperatures (within an ca.100 K range), to Arrhenius at high temperatures – Fig. 3;

(4) Prediction of truly dynamic (temperature scanning rate- or excitation frequency-dependent) responses to e.g. thermal or mechanical excitations – Fig. 4.

These predictions are for a moderately flexible structure, with a crossover frequency of 3.16x 10^6 Hz and minimum activation energy of 40 kJ mol^{-1}.

Materials properties, utilization and design strongly depend on the understanding and accurate prediction of the behaviour under a wide range of temperatures, forced excitations and observation/utilization time scales. Materials properties and dynamics show nearly universal features, that shift and change in predictable ways with conditions and excitation type and intensity. *"Comprehensive and microscopic answers to (1) the surprising and mysterious similarity of the behaviour of different glass formers, (2) the existence of a characteristic*

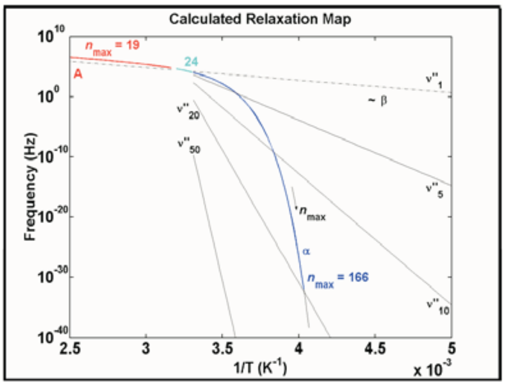

Figure 1. Calculated relaxation map.

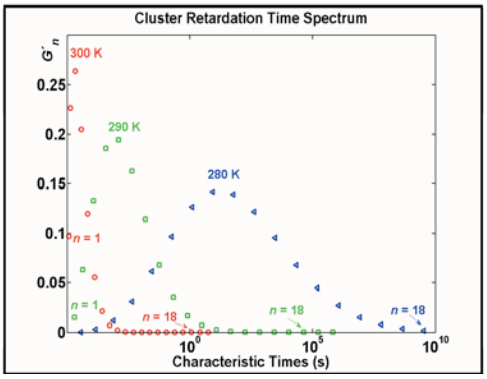

Figure 2. Cluster retardation time spectrum.

José Joaquim C. Cruz Pinto was conceived in an African sub-tropical plain, travelled in rough seas for more than a month and was born in Lisbon, Portugal, in a very conventional city neighbourhood. He dislikes large cities and plains, as much as pure convention, where everything seems set and straightforward - roughness and mountains are his preferred conceptual, sea and landscapes, where things are most interesting and unsettled. Having taught and researched Polymer Science (Thermal and Viscoelastic Behaviour, and Crystallization) and Chemical Engineering (Liquid-Liquid Systems) at the University of Minho for 21 years, he moved to Aveiro 10 years ago, despite its monotonous flatness. His work on those subjects as some of the hobbies concentrate on asking and trying to answer difficult and unconventional questions on a generous range of matters. Walking is his most inspiring exercise. One hobby where he finds questions unnecessary is music.

crossover region, ..., still remain to be invented ...” (E.-J. Donth, The Glass Transition, Springer, 2001) - Cf. Fig. 1.

Materials of any kind, polymers in particular, show complex dynamical behaviour under whatever kind of physical (thermal, mechanical, electrical, …) excitations. When we closely look at the behaviour, what we recognize is the presence of a very large variety of possible and specifiable processes (responses), spanning an extremely wide range of frequencies and cluster sizes within the structure, at any given temperature. Further, that range significantly widens and shifts to lower and lower frequencies (and larger and larger cluster sizes) as the temperature is lowered. No known aspect of materials’ physics contradicts this simple concept, which fits actual observations in very many instances.

So, why not draw on one of the most successful chemical (or chemical physical) theories, on which depends and lives our present and future ability to understand, model and profitably exploit, in both the laboratory and industry, the path and the kinetics of chemical reactions? Many chemists and chemical engineers could be nearly out of business, without the transition state theory (TST)! Transition states (or activated complexes) do physically form and may be detected in even some of the fastest chemical reactions, and expectedly also during many structural motions/rearrangements.

As a TST user, I look at the possible physical processes at the molecular and macromolecular scales in the most general possible way, model their time-, temperature-, and excitation-dependent dynamics, and combine them to realistically and accurately portray their respective roles in materials’ behaviour. For example, in polymers, such motions may involve clusters of widely varying numbers, n, of small chain crankshafts (made of 4 to 6 main chain atoms each).

Further to items (1-4) at the beginning, excellent quantitative agreement with experimental polymer non-linear creep compliance data, D(t), has already been obtained. Extensive quantitative differential scanning calorimetry (DSC) and mechanical spectroscopy (DMA) experiments will be used to validate and refine this *new cooperative segmental theory of materials dynamics* (CSTMD). The theory may be extrapolated to any slow or fast time scales, and explicitly includes the equilibrium (infinite time scale) thermodynamic behaviour.

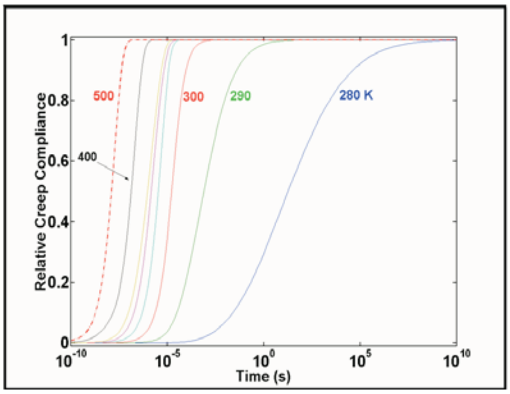

Figure 3. Relative creep compliances.

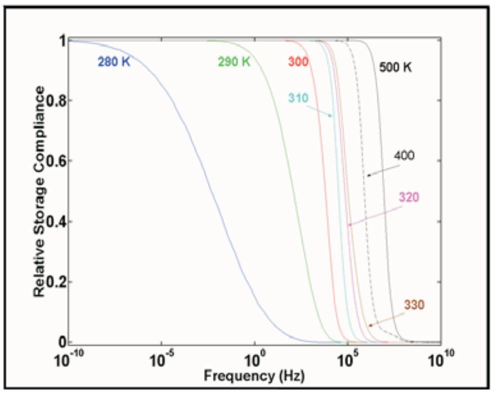

Figure 4. Relative storage compliances.

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PiMM
Pairs in Molecular Materials

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The PiMM approach provides a new methodology to the computational modelling of a solid in terms of the sum of molecular pairs present in the structure, with a significant reduction of the computational effort required.

This new methodology has already been shown to allow a reliable and complete vibrational assignment of interacting molecules in the crystalline form.[1]

This computer-assisted methodology arises within the CICECO Molecular Modelling group aiming at the fulfilment of two goals:

i) to assist the assignment of the experimental spectra (vibrational, electronic, NMR) of molecular materials with known crystal structure.

ii) to allow the prediction of the most probable structure for unknown materials from the experimental spectra, through the identification of the relevant motifs in the potential energy landscape of the solid.

While the first goal has the merit of delivering a new tool for spectroscopists, the second goal is a significant breakthrough in the structural characterization of complex systems from combined ab initio calculations and spectroscopic studies.

The basis of the concept is that intermolecular interactions in the crystal promote perturbations to the isolated molecule spectrum, and these perturbations are additive.

Within this approach, the ith spectroscopic observable s_i of a solid (e.g., vibrational wavenumber, NMR shift, and electronic transition) is given by its calculated value for the isolated molecule, corrected for the perturbations resulting from the contacts with neighbouring molecules in the crystal, Ds_i.

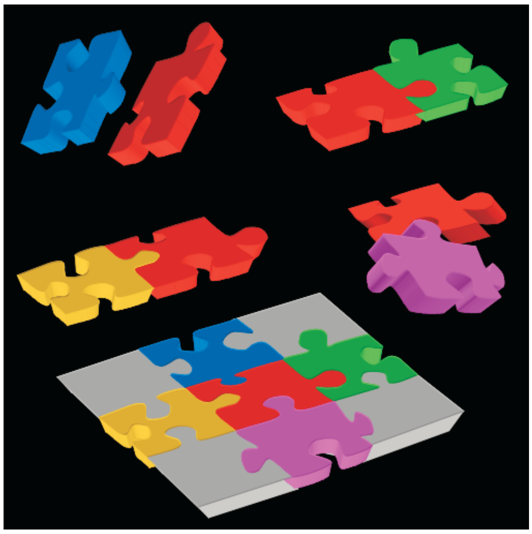

Figure 1. Solving the puzzle by pairs.

Paulo Ribeiro-Claro was born in Viseu (1960), and graduate in “Chemistry” (1984) and Ph.D in “Molecular Sctructure” (1987) at the University of Coimbra, Portugal. Associate Professor at the Department of Chemistry, University of Aveiro, since 2001. Author and co-author of 76 papers in international peer reviewed journals and co-author of a text book for university students. Main scientific interest in “Molecular and Supramolecular Structure”. Also interested in the Public Awarness of Science and Science Popularization. Member of the Portuguese Chemical Society executive board since 2001.

Assuming that only the neighbours in the first shell will significantly affect the spectroscopic observables of the isolated molecule, each spectroscopic observable is given by the simplified equation

$$\sigma_i(crystal) = \sigma_i(isolated) \quad + \quad \sum_{j=1}^{M} \Delta\sigma_i(direct) \quad + \quad \sum_{j=1}^{M} \Delta\sigma_i(indirect)$$

where the term direct refers to the effect of the intermolecular contacts on the atoms involved in the contact (e.g., the effect of a O-H···O hydrogen bond on the O-H vibrational modes), while the term *indirect* refers to the effect of the same contact on the remaining molecule (e.g., the effect of a O-H···O hydrogen bond on the modes involving oscillators in other parts of the molecule), and the summations apply to all possible contacts. The corrections Dsi are obtained from *ab initio* calculations for the relevant molecular pairs.

Since each molecular pair is computed independently, the computer time required to study a cluster of M molecules using this methodology increases with 2^4×(M-1), while with the conventional cluster methods it increases with M^4. For a typical situation of a molecule with 6 relevant neighbours (M=7) the PiMM approach is up to 25 times faster than the cluster approach. However, larger factors are expected, depending on the structure of the solid.

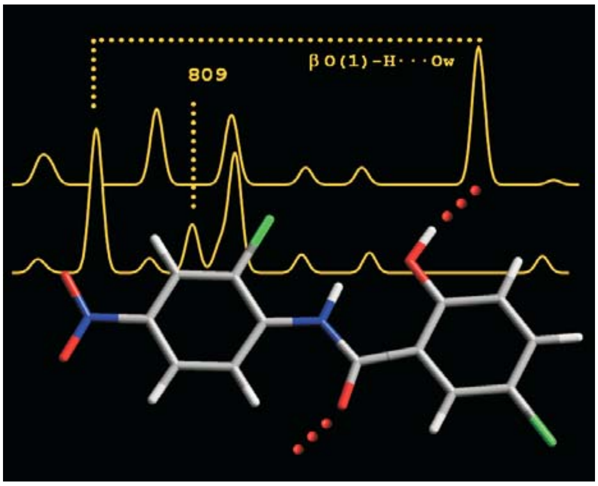

Figure 2. Connecting Structure with Spectra

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Optical Detection of Solid-State Chiral Structures With Unpolarised Light

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In 2006, we have reported the first example of a photoluminescent chiral microporous Ln silicate system (Fig. 1), $Na_3[(Y,Ln)Si_3O_9]\times 3H_2O$ (Ln=Eu, Tb, Er, Ce), in which discrimination between enantomeric domains was achieved by means of Eu^{3+} photoluminescence spectroscopy, using unpolarised light and in the absence of external fields.[1] This enantioselectivity phenomenon may be of importance in the context of fundamental interactions between light and condensed matter.

Zeolites are microporous aluminosilicate materials of considerable industrial importance because they are excellent molecular sieves, ion-exchangers and heterogeneous catalysts. With the advent of the nanotechnology era, and the increasing interest in the use of molecular sieves for device applications, novel zeolite-type materials containing stoichiometric amounts of lanthanide (Ln) metals and exhibiting photoluminescence and magnetic properties have been investigated. The remarkable framework $Na_3[(Y,Ln)Si_3O_9]\times 3H_2O$ is an unprecedented chiral, photoluminescent and microporous Ln silicate system. Only a few zeolite-type silicates exhibit chiral polymorphs, namely zeolite beta and ETS-10,[2] but none of these materials are photoluminescent. The crystal structure of $Na3[(Y,Ln)Si_3O_9]\times 3H_2O$ materials (Fig. 1) displays $(Si_3O_9)_\infty$ chiral spirals interconnected via $\{(Y,Ln)O_6\}$ octahedra, and exhibits a statistical excess of one enantiomer over the other.

Although conventional zeolites are built up of tetrahedral $\{SiO_4\}$ and $\{AlO_4\}$ units, microporous silicates possessing transition-metal heteropolyhedra frameworks are known since the early 1990s. The most prominent member of this new family is titanosilicate ETS-10, containing $\{TiO_6\}$ and $\{SiO_4\}$ units.[2] The constituent elements of heteropolyhedral silicates have been recently extended to the realm of Ln metals, exploring properties such as photoluminescence and magnetism. However, so far, only a handful of microporous (stoichiometric) Ln silicates are known.[3,4]

Previously, chirality sensing involving Ln complexes has been achieved employing magneto-chiral dichroism (MChD)[5] and circular dichroism (CD) methods, such as circularly polarised luminescence (CPL).[6] While CPL measures the difference in emission intensity between left and right circularly polarised light, MChD evaluates the luminescence intensity difference in the directions parallel and antiparallel to an externally applied magnetic field using unpolarised light.

The emission spectra of $Na_3[(Y_{0.7}Eu_{0.3})Si_3O_9]\cdot 3H_2O$ are shown in Fig. 2. Exciting in the O-Eu^{3+} charge-transfer (CT) band doubles the number of emission lines compared with the direct excitation in the Eu^{3+} energy levels. We note that this is only observed between 10 and *ca.* 120 K, the temperature

João Rocha (born 1962) is a correspondent member of the Lisbon Academy of Sciences and Director of CICECO. He got his Ph.D. in 1990 from the Department of Chemistry, Cambridge University, UK and did a one year post-doc in the same group. In 1999 he became Full Professor of Inorganic Chemistry. He is interested in the synthesis of microporous, layered and dense silicates of transition metals and lanthanides (Ln) in the form of powders, membranes and films, and their structural characterisation and applications in catalysis, gas sorption and separation, photoluminescence and magnetism. Other interests: crystalline (MOFs) and amorphous (ureasils…) organic-inorganic hybrids and Ln oxides nanotubes. He has pioneered the development of solid-state NMR of quadrupolar nuclei and he is now also interested in ^1H NMR (FS-LG based) methods for studying hybrids. He published (or has in press) ca. 290 SCI papers, with *ca.* 3300 citations, and 2 patent applications. He is on the editorial board of Eur. J.Inorg. Chem. and Solid State NMR and is member of the Commission on Inorganic and Mineral Structures of the Internacional Union of Crystallography, Portuguese and American Chemical Societies and Materials Research Society. In 2004 he received the Portuguese Science Foundation prize for Scientific Excellence.

Luís António Ferreira Martins Dias Carlos (born 1964) got his Ph.D. in physics from the University of Évora in 1995 working on photoluminescence (PL) of polymer electrolytes incorporating lanthanide (Ln) salts. In 1996 he joined the Department of Physics, University of Aveiro, as Professor Auxiliar. In 1998 he became Professor Associado and in 2004 completed “Provas de Agregação” in Physics. Currently, he is Full Professor. Scientific interests: PL of (i) sol-gel derived organic-inorganic hybrids incorporating Ln ions, (ii) Ln-based micro and mesoporous silicates, (iii) Ln coordination complexes, and small-angle X-ray scattering of organic-inorganic nanostructured multifunctional materials. Luís Carlos has published over 170 SCI papers, with more than 1000 citations, and has been a regular reviewer of leading journals in Physics, Chemistry and Materials Science. He was on the Evaluation Panel for Materials Science Projects, of the Portuguese Science Foundation. He is a member of the European and Portuguese Physical Societies, Materials Research Society and European Rare Earth and Actanide Society. In 2004 he received the Portuguese Science Foundation prize for Scientific Excellence.

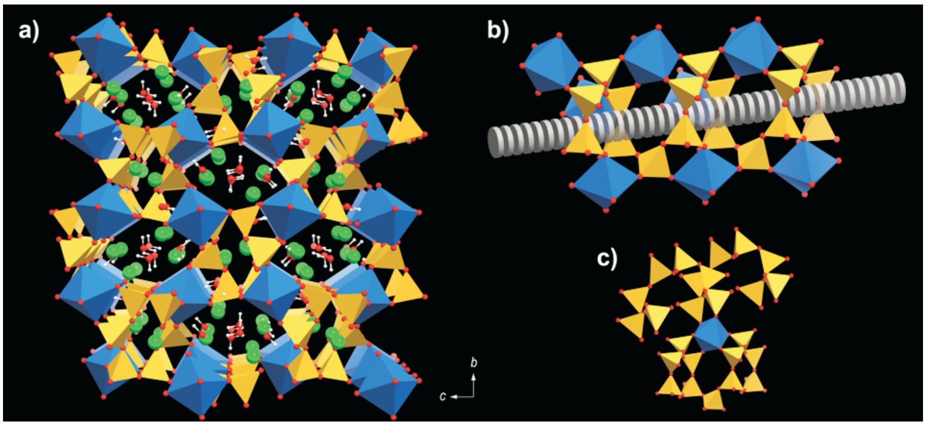

Figure 1. Structure of $Na_3[(Y,Ln)Si_3O_9]\times3H_2O$*. (a) View along the [100] direction of the crystal packing. (b) Portion of the anionic framework showing one* $(Si_3O_9)_\infty$ *spiral chain interconnecting individual* $\{(Y,Ln)O_6\}$ *octahedra. (c) Idealised representation of a* $\{(Y,Ln)O_6\}$ *octahedron connected to two* $(Si_3O_9)_\infty$ *spirals with opposite handedness. Colour code: blue -* $\{(Y,Ln)O_6\}$*; yellow -* $\{SiO_4\}$*; red -* O^{2-}*; green -* Na^+*; white - H.*

range in which the CT band is also detected (despite the fact that the X-ray structure, collected at 100 K, calls for the presence of a single Eu^{3+} site). $^5D_0$ Eu^{3+} lifetime measurements support this conclusion. These observations constitute evidence for the presence of two enantiomers in $Na_3[(Y_{0.7}Eu_{0.3})Si_3O_9]\cdot3H_2O$.

In conclusion, to the best of our knowledge, up to now the discrimination between enantomeric domains has only been achieved using CPL or MChD. Our results raise the exciting possibility that Eu^{3+} photoluminescence spectroscopy may, at least in certain cases, be used to detect and, possibly, quantify enantiomeric domains in chiral frameworks.

Collaborators of this work: D. Ananias, F. Paz (Aveiro) and C. Geraldes (Coimbra).

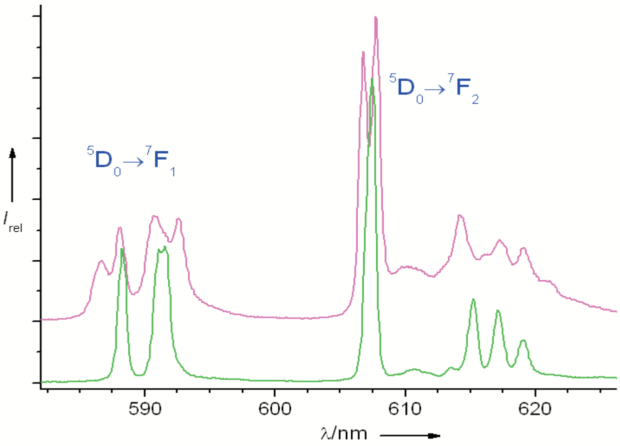

Figure 2. Expansion of the Eu^{3+} $^5D_0 \rightarrow {}^7F_{1,2}$ *transitions (emission spectra) of* $Na_3[(Y_{0.7}Eu_{0.3})Si_3O_9]\cdot3H_2O$*, recorded at 10 K: excited at 526 nm for the* $^5D_1$ *level of* Eu^{3+} *(green line) and at 265 nm, for the charge-transfer band (magenta line).*

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Nanocrystalline Diamond Films on Silicon Nitride Ceramics: Biocompatibility, Tribology, Applications

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Silicon nitride ceramics (SN) were coated with nanocrystalline diamond films (NCD), using hot filament chemical vapour deposition technique (HFCVD). HFCVD technique was optimized in an in-house built reactor. A remarkably high growth rate (~1.5·µm.hr^{-1}) was achieved with HFCVD technique using argon-hydrogen-methane. Crystallite sizes of NCD are in the range 1-30 nm. A bio-active material based on silicon nitride was also successfully coated at low temperature (550 ºC), widening the range of potential applications and forecasting improved biocompatibility of this innovative system.

The combination of NCD and SN results in a highly adherent system with very low friction, high wear resistance and chemical inertness. It can be used in applications as different as mechanical seals, shaping tools for abrasive materials or hip-joint implants. Regarding the latter, every year nearly two million people worldwide are subjected to hip and knee joints replacement. Wear debris particles, originating from material loss of the bearing components, are responsible for severe inflammatory responses leading to aseptic loosening. The deposition of NCD on load bearing surfaces

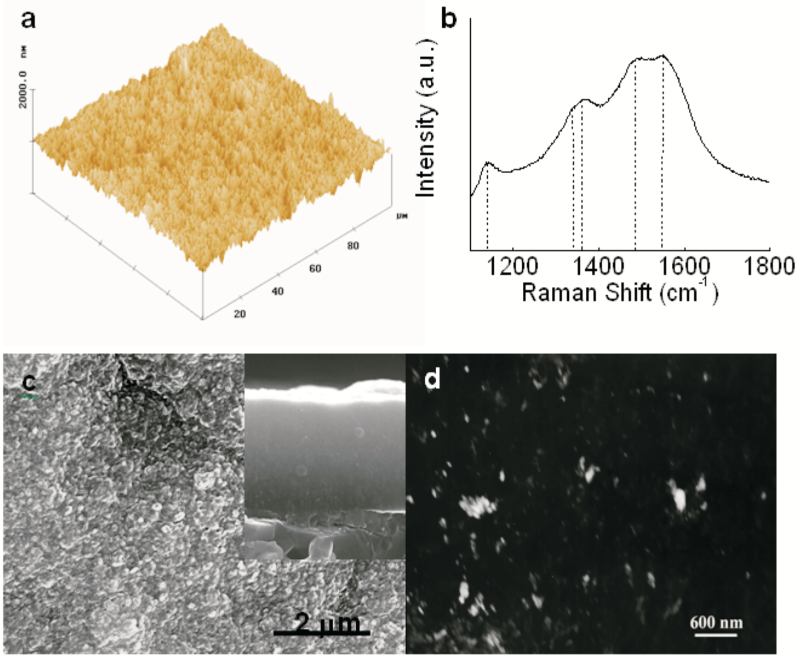

Figure 1. NCD: (a) AFM image; (b) -Raman spectrum; (c), (d) SEM and TEM micrographs.

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Filipe José Alves de Oliveira is a full-time researcher at CICECO. Main current research interest is on nanocrystalline diamond coating of silicon nitride ceramics for tribological applications. A strong emphasis is being put on technological applications and technology transfer. He is co-author of more than 50 papers in SCI journals.

can increase the prosthesis life due to reduced wear response. NCD biocompatible character makes it an ideal choice for biotribological purposes.

The growth of NCD films using HFCVD was a new research subject at the beginning of our study. The key for NCD growth is to increase the secondary nucleation rate of diamond while disabling the growth of the crystallites to sizes reaching the micrometer scale. The coating of SN involves a series of preliminary steps that influence the operating behaviour of the final pieces and starts at the sintering stage and ends with the surface pretreatments. The samples are characterized using techniques such as micro-Raman spectroscopy (-Raman), low incident beam angle X-ray diffraction (LIBAD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The micrographs and graph below are representative of NCD coated SN on what matters film quality (m-Raman) and TEM, and surface morphology (SEM). For the best deposition conditions, mechanical evaluation is done using diamond indentation and potential for practical uses is determined with dynamic tribological tests, where the friction and wear response are obtained. This is done both under un-lubricated conditions and under simulated physiological conditions as a screening test for the potential use of these materials as implants. The clinical success of any implant depends on the cellular behaviour in the interface host/biomaterial. The biological performance of nanostructured NCD coated SN was evaluated using cell cultures of MG63 osteoblast-like cells and human bone marrow cells for assessment of osteoblastic cell growth and osteogenic differentiation. Partly due to surface nanofeatures, NCD films induced human osteoblast proliferation and stimulated specific metabolic activities such as alkaline phosphatase (ALP) activity and matrix mineralization.

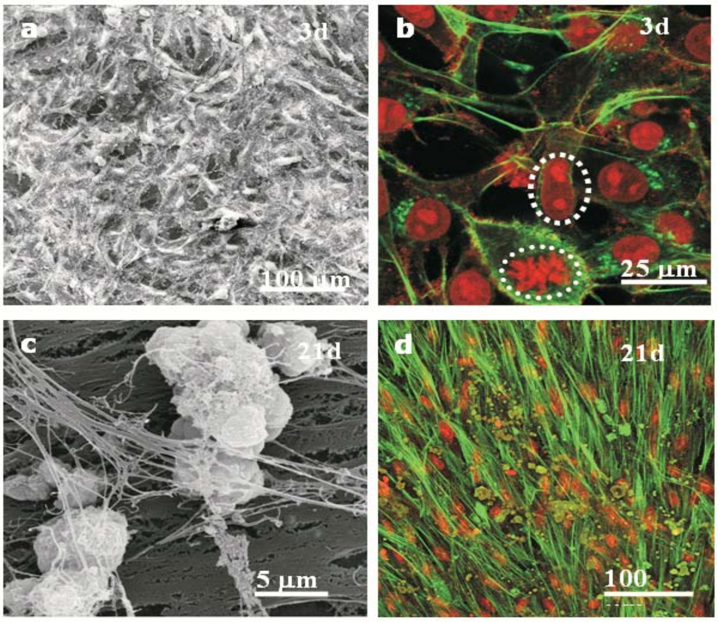

Figure 2. (a,c) SEM and (b,d) confocal laser spectroscopy microscopy (CLSM) of (a,b) MG63 cells cultured on NCD coated Si_3N_4 substrates for different periods of time.

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Nanoengineering Functional Composite Particles

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The dependence of intrinsic properties of materials with size and shape constitutes a major issue in Nanotechnology. Chemistry plays a key role not only in establishing synthetic methods to produce high-quality nanostructures but also in providing strategies to fabricate functional materials using such building blocks. Nature give us examples of materials in which chemical processes have a strict control in determining their final form (Fig. 1) but still remind us of our little understanding on the fundamental behaviour of things at the nanoscale level.

Quantum dots are semiconductor crystallites whose sizes are in the order of a few nanometers thus leading to 3D confinement of electrons (and holes). The evolution of the band structure in a semiconductor, from discrete energy levels present in cluster species, is an important example in the way that size determines the optical properties of solids. Following our previous work in the synthesis of organically capped quantum dots, we have investigated the use of these small particles (less than 5 nm) as nano-fillers to fabricate optically active polymer nanocomposites. In the course of these studies we have reported one of the first examples of an inorganic/polymer nanocomposite prepared via in-situ radical polymerization in a miniemulsion.[1] These nanocomposites are made of polymer beads containing clusters of nanoparticles which still maintain their morphological integrity. This explains the green luminescence observed under UV irradiation, at room temperature, for a nanocomposite containing CdSe quantum dots (red sample) as nano-fillers in a poly(butylacrylate) matrix (Fig. 2, on the left).

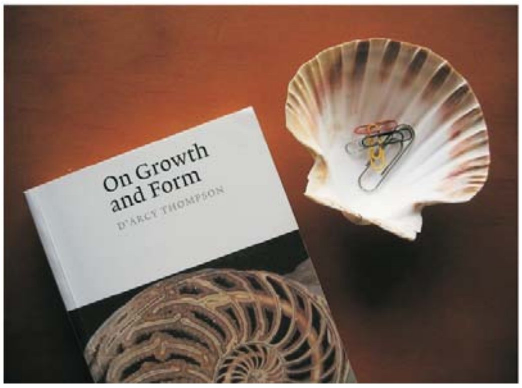

Figure 1. 'On growth and form'

Although the above strategy seems promising to obtain optically active nanocomposites, the replacement of quantum dots incorporating heavy metals (e.g. CdSe) would be clearly advantageous. In this context, we have previously started to develop alternatives to such type of quantum dots by investigating the nanoencapsulation of photoluminescent lanthanide complexes. As an example of this approach, we have reported the synthesis of silica nanocomposites containing an europium (III) complex of 3-hydroxypicolinic acid (Fig. 2, on the right).[2]

Tito Trindade is Associate Professor at the Department of Chemistry of the University of Aveiro and member of the CICECO research unit. Following his PhD at the Imperial College of Science, Technology and Medicine (1996), he has implemented a research line in Nanochemistry at the Department of Chemistry with a special focus in nanostructures for functional materials. Other research interests include the chemistry of inorganic pigments and the synthesis of inorganic-organic hybrids. As part of his academic duties he has been involved in communicating Chemistry for non-specialized audiences, in particular issues related to Nanotechnology.

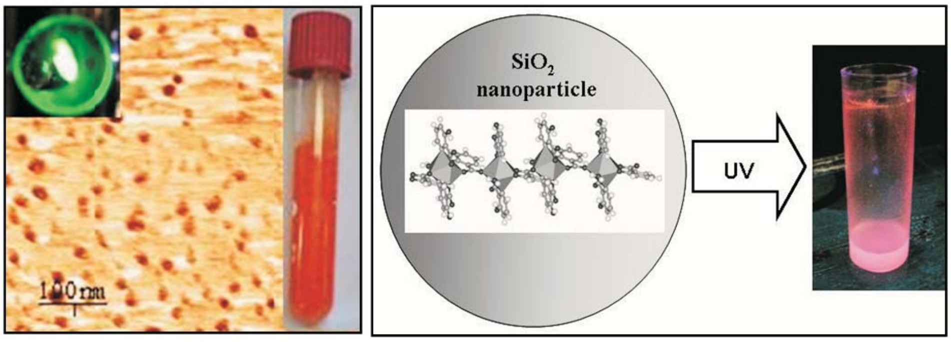

Figure 2. CdSe QD's in a polymer matrix (left) and an Eu(III) complex in SiO_2 beads (right).

This organic ligand acts as an antenna for collecting light and transferring the energy to the lanthanide, originating extensive photoluminescence. This work demonstrated the possibility to synthesise silica nanoparticles containing photoluminescent coordination compounds which once functionalized can be used as nano-fillers to produce polymer nanocomposites, as described above. However this approach is not limited to the encapsulation of luminescent complexes since offers a myriad of possibilities in using other coordination compounds.

Among the several nanostructures produced in our laboratory, the above examples have been selected because they might be regarded themselves as nano-objects for fundamental studies and allow further development of functional nanomaterials. In fact, from this work emerges a general strategy to incorporate in polymers, inorganic nanoparticles with organically capped surfaces. This possibility has been investigated in our laboratories for a range of nanocomposites which after biofunctionalization originate materials with potential interest for in vitro clinical diagnosis, such as biotagging and magnetic separation (Fig. 3).[3]

Direct co-workers: Ana Barros-Timmons, Angela Pereira, Catarina Esteves, Andrei Kholkin, Helena Nogueira, Jorge Guiomar, Luis Carlos, Manuel Silva, Márcia Neves, Paula Santos, Penka Girginova, Rute Ferreira, Teresa Monteiro, Vítor Amaral.

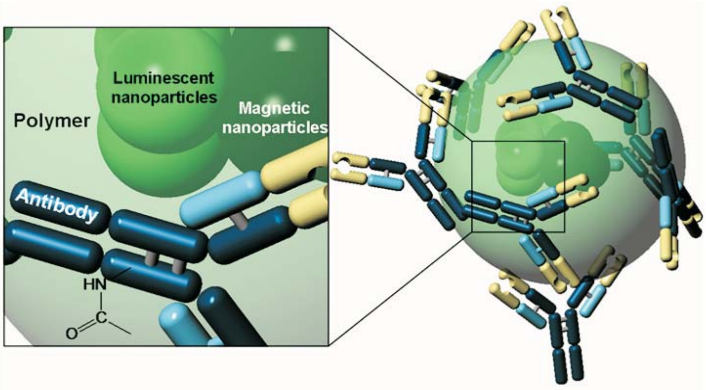

Figure 3. Biofunctionalization of a magnetic/luminescent nanocomposite particle

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Nanoporous Materials For the Production of Furfural From D-Xylose

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We are entering an era of diminishing availability of petrochemical resources used to produce the energy and chemical materials needed by society. Abundant biomass resources are a promising alternative for the sustainable supply of valuable intermediates to the chemical industry. Furfural is a basic nonpetroleum chemical readily accessible from renewable resources, arising from the acid-catalysed dehydration of pentoses, and has a broad industrial application profile, both as a solvent and as a building block for the preparation of tetrahydrofuran, pharmaceuticals, agrochemicals, fragrances and furan based chemicals. Current world production of furfural is ca. 250 metric tons per year. The industrial use of sulfuric acid as the catalyst poses serious operational, safety and environmental problems, and therefore its replacement by alternative "green" non-toxic catalysts is of high priority. Our recent research has been directed towards finding solutions to this problem.[1]

Heteropolyacids (HPAs), presently being used in several industrial processes, are safer to handle, less corrosive and less volatile than conventional mineral acids. Their application in the D-xylose-to-furfural conversion was investigated for the first time in our early work.[2] These experiments were conducted at 413 K under autonomous pressure and with dimethylsulfoxide (DMSO) as solvent. We found that the catalytic performance of Keggin-type heteropolytungstates was on a par with that for sulfuric acid and the commercial sulfonated resin Amberlyst-15. The latter is a solid acid, insoluble in the reaction medium, but degrades at such high temperatures. Comparatively, the HPAs possess higher thermal stability, but they are homogeneous catalysts under these reaction conditions.

Heterogeneous catalysts are generally more stable and more easily separated from the product and recycled than homogeneous catalysts. Attempts have been made to develop heterogeneous catalytic processes for furfural production that offer environmental as well as economic benefits, but to the best of our knowledge none have been commercialized. The evolutionary process for developing improved catalysts demands several critical criteria. Commercial microporous zeolites seem quite promising, but xylose conversion has to be kept low (*ca.* 30%) in order to avoid significant drops in furfural selectivity. At CICECO, we have further investigated D-xylose dehydration over nanoporous solid acids.

A series of composites comprising 12-tungtophosphoric acid immobilized in micelle-templated silicas (e.g. MCM-41) with large unidimensional mesopores were prepared by either incipient wetness impregnation (Fig. 1) or immobilization in amino-functionalized silicas.[3] These materials exhibited higher activity than the bulk HPA and furfural yields were similar to those obtained with H_2SO_4, under similar reaction conditions (58%, at 433 K). Strong host-guest interactions and active site isolation for the materials with low HPA loadings (15 wt.%) and the amino-functionalized supports appeared to benefit activity and stability with DMSO as solvent.

Anabela Valente is Full-Time Researcher at CICECO. She has worked at the University of Aveiro since receiving her Ph.D. degree in Chemical Engineering in 2000 from Universidade Nova de Lisboa. She brought experience in catalysis, from homogeneous to heterogeneous, to CICECO.

High boiling DMSO requires difficult and energy-intensive isolation procedures. Water is cleaner and cheaper, but xylose dehydration is sluggish with water as the solvent. Recent advances have shown that improved results are possible in biphasic systems consisting of water and toluene (W/T), allowing the continuous extraction of furfural from the aqueous phase (Fig. 2). However, for the supported heteropolyanion catalysts, we observed significant leaching of the HPA from the support into the aqueous phase during reaction at high temperatures, which constitutes a major limitation for any potential industrial application.

An approach to increase stability towards leaching is to prepare catalysts with covalently bonded acid groups. We prepared surfactant-templated micro-mesoporous silicas with covalently bonded sulfonic acid groups and large specific surface area (Fig. 1).[4] At 443 K, furfural selectivity was 78%, at > 85% xylose conversion, which is an improvement relatively to commercial zeolites. However, after long residence times the hybrid catalysts deactivate due to surface loading with organic products, and thus far it has not been possible to efficiently regenerate them. Thermal processes require temperatures higher than the thermal stability of the sulfonic surface groups (523 K).

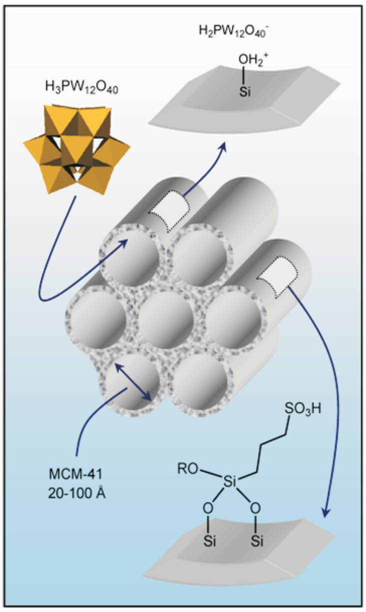

Figure 1. Representation of the ordered mesoporous silica MCM-41 and two of the methods used to prepare solid acid derivatives.

Water-tolerance is a critical factor for operating in a biphasic water-toluene system at elevated temperature. Generally, water has a negative effect on the acid properties of metal oxides. Unusual behaviors have been reported for some niobium-based solid acids, which show high acid strength in spite of the water content. We found that microporous AM-11 crystalline niobium silicates and ordered mesoporous MCM-41-type niobium silicates (in the H^+-form) are active catalysts for xylose dehydration in W/T at 433 K, yielding up to 50% furfural within 6 h reaction.[5] For the Nb-MCM-41 materials partial loss of activity in recycling runs and leaching of Nb from MCM-41 occurred during the reaction. In contrast, crystalline AM-11 materials are more water-tolerant and can be recycled without loss of activity and selectivity. Furthermore, furfural selectivity above 80% conversion was higher for AM-11 than for Nb-MCM-41 materials. More recent results have shown that aluminium-containing MCM-41 catalysts are more stable towards leaching than the reported Nb-MCM-41 materials.

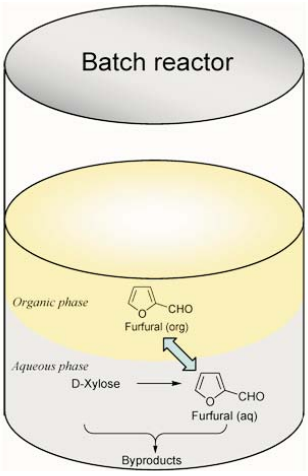

Figure 2. Batch process for production of furfural from D-xylose. The stirred reactor was charged with toluene, water, D-xylose, powdered catalyst, and purged with

Crystalline layered metal oxide cation exchangers, such as titanates, niobates and titanoniobates, are potentially strong solid acids when in the H^+-form. However, the high charge density of the anionic sheets in these materials hinders the access of bulky substrate molecules to the acid sites. This problem has recently been addressed by exfoliating the layered metal oxides to give aggregates of nanosheets, where the two-dimensional sheet structure remains (Fig. 3). The composites have much higher specific surface areas than the acid-exchanged layered precursors and function as strong solid acid catalysts, rivaling or even beating niobic acid, which is a rare water-tolerant solid acid. We found that they are more active and somewhat more selective catalysts than the microporous AM-11 crystalline niobium silicates, which in turn yielded more furfural than zeolites, such as HY and mordenite (Si/Al 6), under similar reaction conditions.[6] Furthermore, no metal leaching occurs and furfural yields remained practically the same in recycling runs. Adjustment of the reaction conditions, such as temperature and residence time, together with reactor design could open up valuable perspectives in the application of transition metal oxide nanosheets to the conversion of xylose into furfural. There are many other factors that have to be assessed before any of these materials can be proposed as an attractive catalyst for an existing commercial process. Nevertheless, these early laboratory data are promising.

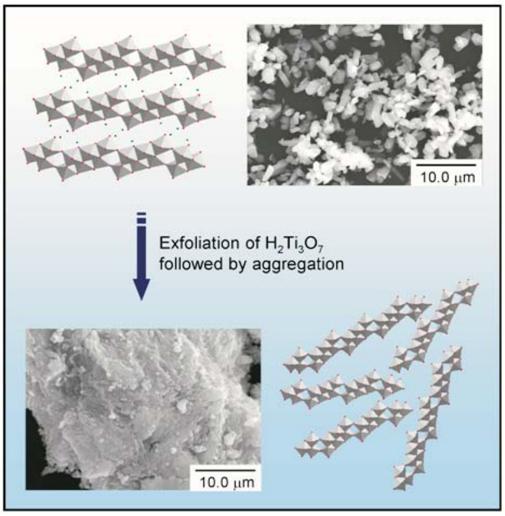

Figure 3. Structural representations and SEM mages of $H_2Ti_3O_7$ before and after the exfoliation-aggregation process.

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PZT Films On Optical Fibers: New Opportunities For Optoelectronics and Nanooptics

A wide range of opportunities exist for the use of active fiber coatings for the development of miniature electrically controlled devices for optoelectroncis. This is especially important for telecommunications, fiber optic sensor networks, and a variety of other applications where optical fibers are used. The function of an active coating based on the piezoelectric thin film is to provide and electrical means for controlling the optical response of a section of a fiber underlying the active coating. The converse piezoelectric effect excited in the film can be used to achieve high stress and, via this stress to modulate the phase shift of the propagating light. Along with this effect, the mechanical motion of the fiber is possible [1] thus transforming the device into nanoactuator with the displacement level of the order of 1 m. These actuators can be used in optical alignment systems, scanning optical microscopes, and also in the area of nanooptical devices where high resolution and scalability is a must. Previous attempts to built fiber optic actuators encountered many problems, the most important is the low piezoelectric properties of ZnO and necessity to control its orientation (no poling is possible). We used a hybrid technology developed in CICECO,[2] to deposit thick $Pb(Zr,Ti)O_3$ (PZT) films on standard telecom fibers. Such coating will find a broad range of applications, in which displacement of the fiber tip is a useful function. WE now describe our recent progress on the design and fabrication of piezoelectric coatings on optical fibers.

Composition and microstructure design. The high piezoelectric properties of PZT solid solutions are useful for actuator applications only if a tight control of the composition and orientation is achieved. Also, a stress caused by the thermal expansion coefficient mismatch is a problem. To overcome these difficulties special buffer and electrode layers were designed, allowing crack-free films to be deposited (Fig. 1). The used hybrid sol-gel route allowed incorporating of pre-sintered PZT particles that are 'glued' by the sol-gel solution. Multiple infiltration procedure was applied to remove undesired porosity and decrease the roughness of the coating.

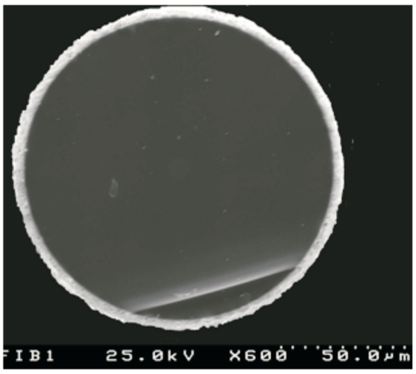

Figure 1. SEM picture of a coated fiber.

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Paula Vilarinho is an Associate Professor at UA since 2000. She got her PhD degree from UA in 1994. Present R&D interests include the synthesis and characterization of nanoparticles, nanostructures, thin and thick films of dielectric, piezoelectric and ferroelectric materials for microelectronic and biomedical applications. She has been involved in 15 national R&D projects and 13 European R&D actions, networks and projects on the development and characterization of dielectric, piezoelectric and ferroelectric materials. She has supervised 12 Post-Doc and 10 Ph.D. works. She has edited 4 books, published 3 book chapters, over 120 papers in SCI journal and one patent. She has been collaborating with more than 12 Portuguese and 10 foreign R&D groups. She organised 5 international scientific meetings and 4 National and International workshops on materials.

Electrode design. Symmetrical electrodes do not allow flexural bending, a problem which was alleviated by a suitable electrode patterning (semicylindric electrodes), so that the stress could be applied only on one side of the fiber (Fig. 2). The displacement level was controlled by the length and the electrodes surface area.

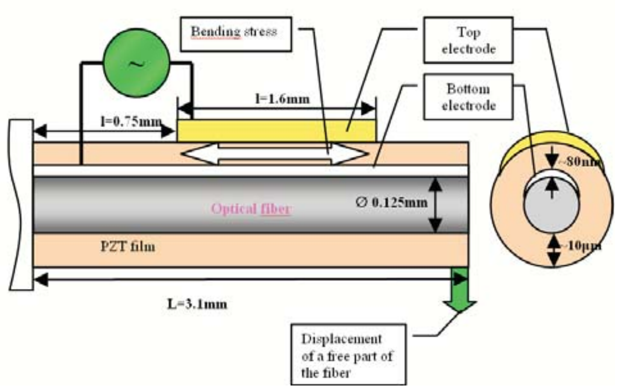

Figure 2. Schematic of the electrode design for fiber-optic flexural actuator.

The device could be used even two orthogonal displacement are needed. The photograph of the device is shown on Fig. 3, where the wiring to the top electrode is seen. The displacement could be monitored by the specially designed measurement system based on the photonic sensor.[3] The measurements of the displacements (Fig. 4) were complemented by the finite element modeling of the piezoelectric element in the cylindrical geometry and the results of the measurements (level of displacement, resonance pendence on geometrical parameters) were close to the calculations.[4] The maximum displacement level at resonance is about 800 nm (Fig. 4) but it can be further increased by appropriate poling and choice of suitable filler (PZN-PT instead of PZT).

This work was carried out in collaboration with Dr. Andrei Kholkin.

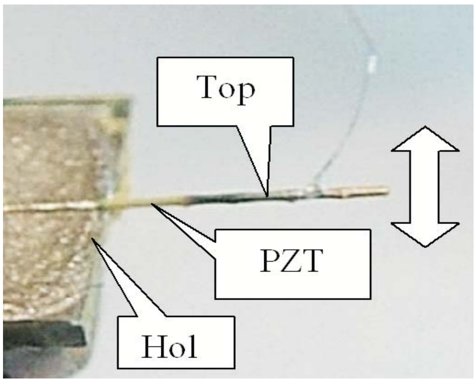

Figure 3. Photograph of the fiber-optic actuator.

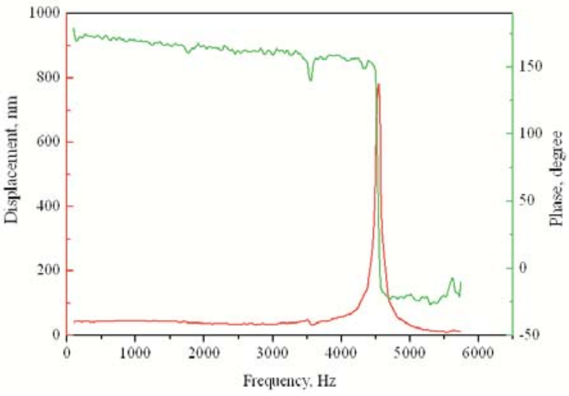

Figure 4. Representative frequency dependence of the piezoelectric response of the fiber driven at V_{ac}=5 V.

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Small Particles Have Large Impact: Fabrication of Ferroelectrics Via a Composite Sol-Gel Ferroelectric Thin films: What For? Are There Any Limitations?

By 2007, flash memory is expected to be a $43 billion industry. Because flash memory can store data even when batteries are removed from a device, cutting off the power supply, flash is a key element in millions of cellular phones, handheld’ (in CNET News by Michael Kanellos).

Ferroelectric materials find various applications in an extraordinarily broad range of advanced microelectronic components. $PbZr_{1-x}Ti_xO_3$, (PZT) is the core of "non-volatile" memory cells in silicon-based technology that do not lose information when power is switched off. $Ba_{1-x}Si_xTiO_3$ (BST), an environment compatible system, is a promising lead-free dielectric material for Dynamic Random Access Memories and low cost agile microwave circuits (phase shifters, tunable filters and matching network). The processing temperature is a key parameter in ferroelectric film fabrications. It ensures phase purity, controls interdiffusion between the film and underlayers, which have a direct impact on film’s final properties. The high processing temperatures and relatively oxidizing atmospheres necessary for ferroelectrics led to the traditional use of noble metal electrodes in conjunction for practical applications. Low processing temperature has broad implications, opening up the possibility of low-cost, high-conductivity copper foils for a range of perovskite materials, including ferroelectric films embedded in printed circuit board (PCB) applications for capacitors, varactors, sensors and multilayer piezoelectric stacks (Nature Materials, 4, 233, 2005). However, low cost metallic foils as substrates for films poses several important problems. Success depends on finding fabrication conditions that fulfil oxidation and crystallization temperature requirements. The development of a single phase perovskite microstructure in PZT based and BST films at low temperatures is critically important. A low annealing temperature is also essential when glass or polymeric substrates are required.

How to overcome these limitations? Our contribution

We developed a new methodology based on chemical solution deposition (CSD) of a diphasic precursor in which perovskite nanometric particles dispersed in the amorphous precursor sol were used as seeds to promote the nucleation of the perovskite phase at low temperatures. Improved electric properties were obtained in these low temperature-processed films. In the following, our achievements in the area of nano-suspension delivered ferroelectric thin films are briefly presented.

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Paula Vilarinho is an Associate Professor at UA since 2000. She got her PhD degree from UA in 1994. Present R&D interests include the synthesis and characterization of nanoparticles, nanostructures, thin and thick films of dielectric, piezoelectric and ferroelectric materials for microelectronic and biomedical applications. She has been involved in 15 national R&D projects and 13 European R&D actions, networks and projects on the development and characterization of dielectric, piezoelectric and ferroelectric materials. She has supervised 12 Post-Doc and 10 Ph.D. works. She has edited 4 books, published 3 book chapters, over 120 papers in SCI journal and one patent. She has been collaborating with more than 12 Portuguese and 10 foreign R&D groups. She organised 5 international scientific meetings and 4 National and International workshops on materials.

Isabel Miranda Salvado is an Associate Professor at UA since 2003. She started her research activities in sol-gel field in 1984 with the preparation of glassy materials. Since then she prepared mullitic compositions and studied the preparation of composite materials with glass matrix. Her current research interest include sol-gel preparation and characterization by several techniques including Small Angle Neutron Scattering and Positron Anhiilation Spectroscopy of inorganic and hybrid organic-inorganic materials as bulk, thin films and fibers for different applications: ferroelectrics, anti-corrosion, biomedicals. She has published ca. 60 technical papers in these fields. She collaborated in several scientific projects in recent years.

Structural and electrical properties of nanoseeded PZT and BST thin films

200-300 nm thick PZT (52/48) and BST (80/20) films on Pt/Ti/SiO_2/Si substrates were prepared from sol precursors with the addition of nano particles (20-80nm in size and 0-5 mol.% in concentration). Single phase perovskite PZT thin films were obtained at 410 ºC when 5 mol% nano-particle seeds were used (600-700 ºC is required if without seeds). Single phase perovskite BST thin films were obtained at 600 ºC when 5 mol% nano-particle seeds were used (700 -850 ºC is required if without seeds). Due to the presence of nanometric particles seeded films exhibit enhanced crystallization kinetics and the overall activation energy for the perovskite crystallisation was reduced from 219 kJ/mol for the unseeded to 146 kJ/mol for the 5 mol% seeded PZT films and reduced from 189 KJ/mol for the unseeded to 80 KJ/mol for 5 mol% seeded BST films.

The multi-locals for crystallization of perovskite phase drastically change the microstructure and subsequently improve dielectric response. The transient Pt_xPb phase was suppressed in seeded PZT films during the pyrolisis (Fig. 1) which improves the interface sharpness. Seeded PZT films pyrolysed at 430 °C show typical ferroelectric properties (Fig. 2) which are well-suited for applications in which glass, metallic or polymeric (such as polyimide family type) substrates are required. Superior dielectric properties were obtained in seeded BST (80/20) films annealed at 650 ºC (Fig. 3). One particular important consequence of the utilization of nanoparticles is related with the increase of fatigue resistance of seeded films (Fig. 4).

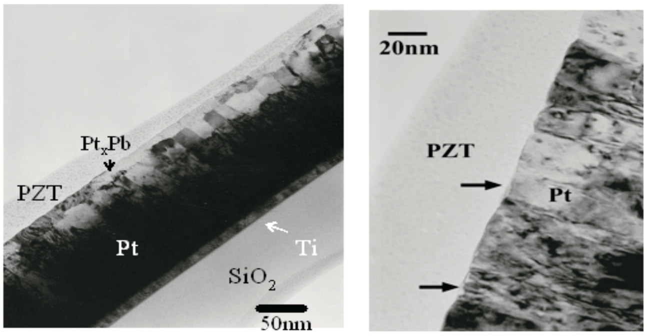

Figure 1. TEM cross section of PZT unseeded (a) and seeded (b) films pyrolyzed at 400 ºC 15 min.

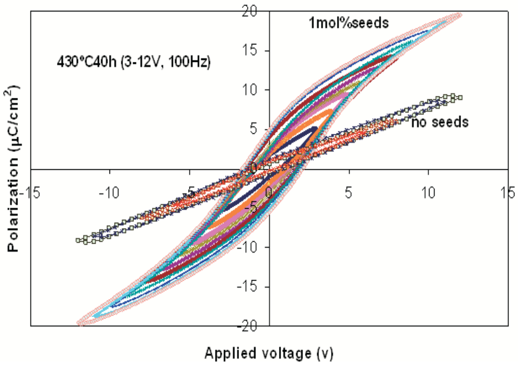

Figure 2. Hysteresis loops of PZT unseeded and seeded films after pyrolysis at 430 ºC for 40 hours.

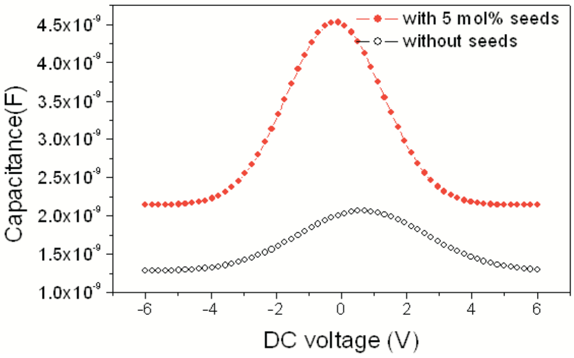

Figure. 3 C-V curves of BST thin films with various seeds annealed at 650

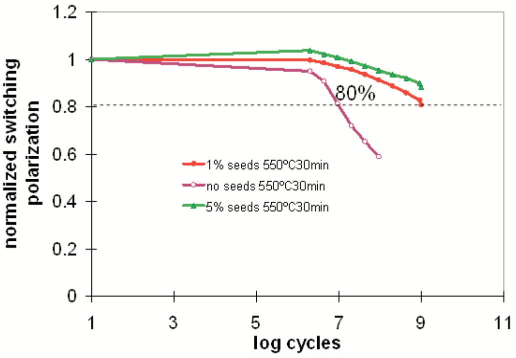

Figure 4. Normalized switching polarization versus the number of switching cycles for seeded and unseeded PZT films.

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